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FURTHER MEASUREMENTS OF THE
EFFECT OF PRESSURE ON THE
ELECTRICAL RESISTANCE OF
GERMANIUM

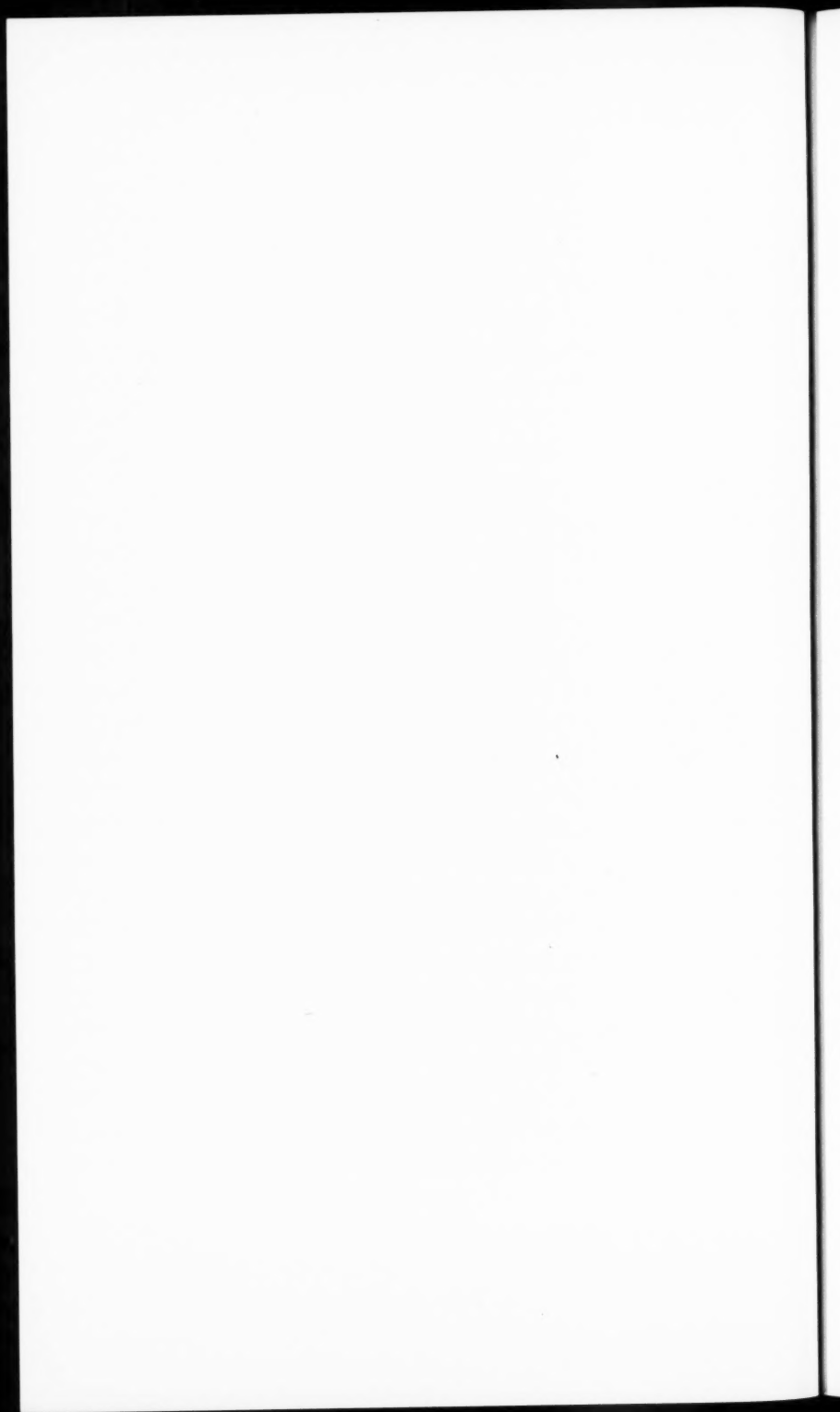
By P. W. BRIDGMAN

MISCELLANEOUS MEASUREMENTS
OF THE EFFECT OF PRESSURE
ON ELECTRICAL RESISTANCE

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THE EFFECT OF PRESSURE ON
SEVERAL PROPERTIES OF THE ALLOYS
OF BISMUTH-TIN AND OF
BISMUTH-CADMIUM

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INTRODUCTION

In two recent papers¹ I have presented measurements of the effect of pressure on the resistance of germanium: in the first paper the pressure range was 30,000 kg/cm² with a true liquid as a pressure transmitting medium; in the second paper the pressure range was 100,000 kg/cm² and the transmitting medium silver chloride. In both cases the measurements were made at room temperature, this being necessitated by instrumental limitations. It was recognized that it would be desirable if measurements could be extended to temperatures in the intrinsic range. This paper presents such an extension, but at the cost of a considerable reduction in the pressure range. Apparatus was at hand which had been previously used² in resistance measurements to low temperatures. In this apparatus pressure was transmitted by nitrogen, the use of a gas having been necessitated in order to avoid the freezing under pressure which would have occurred if pressure had been transmitted by a liquid. Nitrogen gas is also adapted to be the medium at high temperatures, avoiding now difficulties arising from the chemical decomposition or other activity of a transmitting liquid.

The former apparatus was used with no essential modification. This apparatus consists of an upper cylinder, maintained at room temperature, in which is the manganin pressure gauge and the in-

ulating plugs connected to the specimen to be measured. The upper cylinder is connected with a tube to the lower cylinder, in which is mounted the specimen to be measured, the connections to which are taken out through the connecting tube to the insulating plugs in the upper cylinder. The potentiometer method of measuring resistance was used, necessitating four leads for the specimen. The lower cylinder is kept at the desired temperature and thermostatically controlled. The temperature range was from 0°C to 200°C , the latter being above the intrinsic temperature of any of the specimens. The pressure range was kept at $7,000\text{ kg/cm}^2$ in the interests of safety, the pipe connections being of the mushroom unsupported area type with a somewhat nebulous safety limit. The source of the nitrogen was a commercial cylinder under ordinary commercial pressure, maximum about 2,000 psi. Two intensifiers with a suitable system of valves permitted charging the high pressure apparatus to an initial pressure of $2,000\text{ kg/cm}^2$. Pressure above 2,000 was reached with a single stroke of the high pressure piston.

The germanium I owe, as before, to the courtesy and interest of Dr. William Shockley of the Bell Telephone Laboratories. Measurements are here presented in the $0^{\circ} - 200^{\circ} - 7,000\text{ kg/cm}^2$ range for four specimens, three of them new, of n-type germanium of specific resistances at room temperature of 34.9, 11.3 (old), 6.6, and 0.004 ohm cm , and on three specimens, two of them new, of p-type, of specific resistances at room temperature of 2.1, 1.5 (old), and 0.00079 . The n-type specimens will be referred to as Nos. 1, 2, 3, and 4 respectively, and the p-type as Nos. 5, 6, and 7. The range of intrinsic resistance in these specimens is considerably greater than before, so that we are here concerned with an essentially three parameter problem, that is, with the resistance of germanium as a function of pressure, temperature and degree of purity. In addition to measurements in the $7,000\text{ kg/cm}^2$ range, measurements to $30,000\text{ kg/cm}^2$ at room temperature were made on the three new n-type specimens and the two new p-type specimens, and in addition on a new n-type specimen of specific resistance 0.24 (No. 8) and two new p-type specimens of specific resistances 0.87 and 0.93 (Nos. 9 and 10). No attempt was made to repeat the former measurement to $100,000\text{ kg/cm}^2$ on any of the new material, the internal evidence of the former measure-

ments having been that strain effects due to the non-hydrostatic medium are particularly large and difficult to interpret for germanium. I believe, however, that the strikingly anomalous effects above 30,000 must be kept in mind for any complete theory of the pressure effects.

The only new problem of technique which requires mention was connected with insulation at the higher temperatures. This problem was satisfactorily solved by the use of "Ceroc-T" wire from the Sprague Electric Co. (double teflon-ceramic coated) for the leads through the connecting pipe. In the lower cylinder proper insulation was secured with sheet teflon, which I owe to the courtesy of the DuPont Co., disposed at strategic situations. In all cases measurements were made by the potentiometer method with four leads. These were soldered into fine grooves cut transversely of the specimen. Pure tin was used for solder, the melting point of ordinary lead-tin solder being too low. The specimens were in the form of rods of square section, of the general order of dimensions of 2 cm long by 3 mm square, and were cut from single crystals. In the following, results are given in terms of specific resistance. These specific resistances were calculated from the measured resistances and the dimensions at room temperature and atmospheric pressure, disregarding changes of dimensions arising from temperature or pressure changes. Any corrections for such changes of dimensions are small and within errors of reproducibility of the material, there being measurable differences of specific resistance in specimens cut from the same original crystal.

THE RESULTS

A. Resistance to 200°C and 7,000 kg/cm².

The principal objective in making measurements at higher temperatures was to get the temperature into the intrinsic range, that is, the range where the primary contribution to the conductivity is provided by the germanium rather than the impurity. Entrance into the intrinsic range is roughly marked by reversal of the sign of the temperature coefficient of resistance, in the intrinsic range resistance decreasing with rising temperature, whereas at lower temperatures where conductivity is provided predominantly by

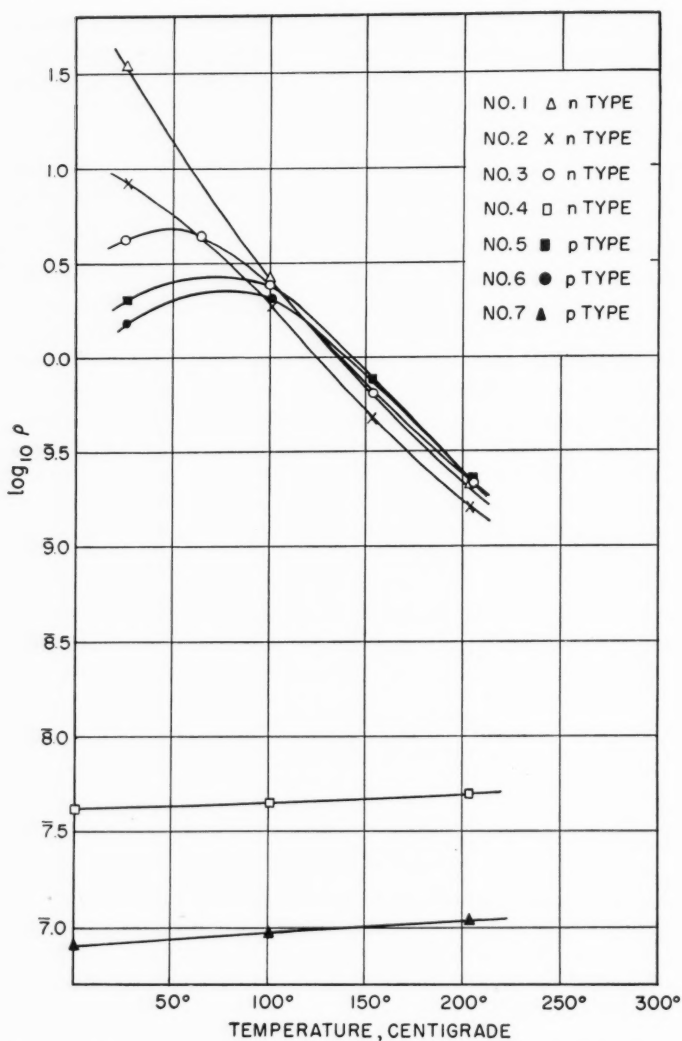


Figure 1. The specific resistance at atmospheric pressure of several specimens of germanium as a function of temperature. The specimens may be identified from the description in the text.

the impurity resistance increases with increasing temperature. The expectation was that in the intrinsic range the effect of pressure on resistance would be independent of the type of impurity that imparts the conductivity at lower temperatures, i.e., the same for n- and p-types. Of course this is to be expected only

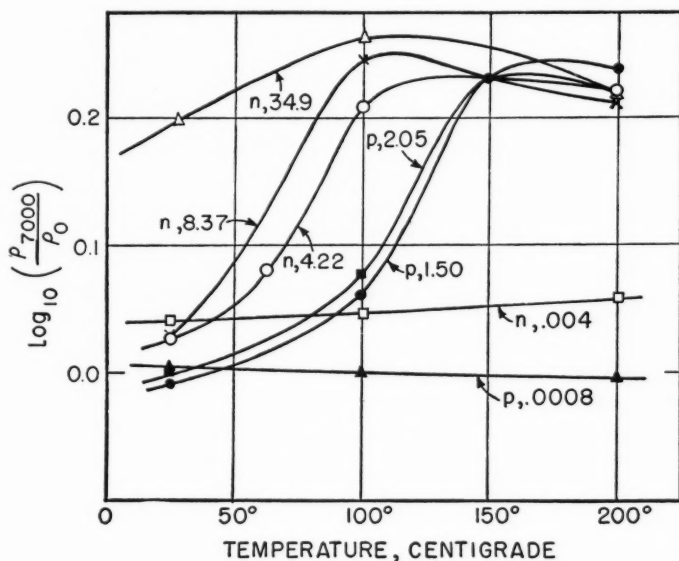


Figure 2. The logarithm of the ratio of resistance at 7,000 kg/cm² to that at atmospheric pressure as a function of temperature for various specimens of germanium. The labels on the individual curves indicate whether n- or p-type and the specific resistance at room temperature in ohm cm.

within reason, in a range where the impurity is not present in such excessive amount as to swamp the effect of the germanium itself. This expectation was gratifyingly fulfilled.

In Figure 1 is shown the logarithm of the specific resistance at atmospheric pressure of the various specimens as a function of temperature. The five specimens of which the specific resistance at room temperature varies from 1.6 to 34.9 roughly agree above

100°, that is, above 100° these specimens are in the intrinsic range. The two very heavily doped specimens of initial specific resistances 0.004 and 0.0008, however, are obviously of a different type, the conductivity of the impurities greatly preponderating over that of the germanium up to 200°. These specimens would be expected to become intrinsic, if at all, only at considerably higher temperatures.

With regard to behavior under pressure, the expectation is that the five upper specimens of Figure 1 will behave approximately the same above 100°, but that there is no reason why the other two, heavily doped, should exhibit similar behavior in our range. Figure 2 shows the behavior under pressure. The complete pressure behavior of the five specimens with specific resistance greater than 1 can be reproduced in this figure because the relation between pressure and logarithm of resistance is linear in pressure for all five, so that a single parameter suffices to reproduce the pressure behavior. The parameter thus exhibited in Figure 2 is $\log_{10}(R_{7000}/R_0)$. The pressure behavior of the two heavily doped specimens is, however, not linear in pressure, so that it cannot be reproduced by a single parameter. In order to permit a rough qualitative comparison, however, the same parameter is shown in Figure 2 for these two specimens also. Their behavior in detail under pressure will be described in the next paragraph. The figure shows in the first place that above 150° the effect of pressure on resistance of all five moderately doped specimens is approximately the same, as was expected. This effect is an increase of resistance under 7,000 by roughly $\log^{-1} 0.22$, or by $1/6$, making the average pressure coefficient of resistance 2.4×10^{-5} . At room temperature the p-type specimen of resistance 1.5 has a small negative pressure coefficient, whereas the other p-type specimen of resistance 2.05 shows no measurable effect of pressure. The n-type specimens at room temperature show a smaller positive pressure coefficient than at higher temperature, the smaller the specific resistance (that is, the greater the amount of impurity) the smaller the coefficient. A short extrapolation indicates that the pressure coefficients of the 6.6 and 11.3 specimens will become negative at temperatures not far below 0°C. The pressure coefficient of the purest n-type specimen, of resistance 34.9, is not far from constant over the entire temperature range. All five specimens show a

maximum pressure coefficient between room temperature and 200° , the indications being, therefore, that at still higher temperatures the pressure coefficients will become progressively less. However, extrapolation to an eventual reversal of sign at much higher temperatures would obviously be hazardous.

The numerical results shown in Figure 2 are reproduced in Table I for the five moderately doped specimens, and in Tables II

TABLE I

EFFECT OF PRESSURE ON RESISTANCE IN $7,000 \text{ kg/cm}^2$ RANGE

Specimen	Temperature $^{\circ}\text{C}$	$\log_{10} \rho_{7000} / \rho_0$
	n-type	
No. 1 $\rho_{27^{\circ}} = 34.9$	27°	+0.197
	99.6°	+0.260
	199.9°	+0.213
No. 2 $\rho_{26^{\circ}} = 8.37$	26°	+0.030
	100.0°	+0.242
	150.0°	+0.231
	200.0°	+0.214
No. 3 $\rho_{25^{\circ}} = 4.22$	25.2°	+0.026
	64.3°	+0.080
	99.8°	+0.207
	149.9°	+0.228
	200.2°	+0.219
No. 4 $\rho_0 = 0.00410$	0°	+0.0412
	100.2°	+0.0474
	199.7°	+0.0600
	p-type	
No. 5 $\rho_{25^{\circ}} = 2.05$	25.1°	.000
	100.0°	+0.078
	149.7°	+0.229
	200.6°	+0.218
No. 6 $\rho_{25^{\circ}} = 1.505$	25°	-0.009
	100.0°	+0.060
	149.9°	+0.230
	200.2°	+0.237
No. 7 $\rho_0 = 0.000794$	0°	+0.00280
	100°	-0.00045
	200°	-0.00363

TABLE II
EFFECT OF PRESSURE ON RESISTANCE OF
No. 4 n-type GERMANIUM

Pressure kg/cm ²	0°	log ₁₀ ρ 100.2°	199.7°
0	7.61278	7.63949	7.69810
1,000	7.61753	7.64390	7.70448
2,000	7.62151	7.64962	7.71115
3,000	7.62801	7.65569	7.71888
4,000	7.63390	7.66266	7.72762
5,000	7.64025	7.67013	7.73704
6,000	7.64693	7.67827	7.74713
7,000	7.65390	7.68688	7.75804

TABLE III
EFFECT OF PRESSURE ON RESISTANCE OF
No. 7 p-type GERMANIUM

Pressure kg/cm ²	0°	log ₁₀ ρ 100°	200°
0	6.89980	6.97110	7.03930
1,000	6.90020	6.97059	7.03863
2,000	6.90060	6.97020	7.03802
3,000	6.90100	6.97002	7.03748
4,000	6.90140	6.97006	7.03697
5,000	6.90180	6.97019	7.03649
6,000	6.90220	6.97039	7.03606
7,000	6.90260	6.97067	7.03565

and III for the heavily doped non-linear specimens. It will be seen that the behavior of these two latter specimens, one of n- and the other of p-type, is quite different. One point of similarity, however, is the relatively small absolute magnitude of the pressure effect over the entire temperature range. The p-type specimen, of specific resistance 0.000794, increases linearly with pressure over the 7,000 range at 0°. At 100° it initially decreases in resistance, with a flat minimum near 3,000 kg/cm², and an eventual rise above 3,000 at a slower rate than the initial drop. At 200° the resistance decreases up to 7,000 approximately linearly, but with recognizable upward curvature, and with approximately the same absolute value of the coefficient as at 0°. The n-type specimen of

specific resistance 0.00410 at 0° increases in resistance at all three temperatures, in all cases approximately linearly, but in all cases with recognizable upward curvature. The curvature and the average value of the coefficient become larger at the higher temperatures.

B. Resistance to $30,000 \text{ kg/cm}^2$ at Room Temperature.

Room temperature, being below the intrinsic range for all except perhaps specimen No. 1, no similarity is to be expected between the behavior of n- and p-types, and the results will be presented separately. In Figure 3 is given in a single diagram the effect of pressure to $30,000$ on the logarithm of the specific resistance of four n-type specimens. Over a range of specific resistance of four powers of ten the sign of the effect is the same, namely an increase of resistance with pressure. This increase, furthermore, is not linear, but increases with marked acceleration beyond $10,000$ or $15,000 \text{ kg/cm}^2$. The final total increase under $30,000$ increases consistently with the absolute value of specific resistance. The initial rate of increase in the linear range does not, however, show any consistent variation with absolute value of specific resistance.

The specimen of highest purity, No. 1, exhibits marked deviation from linearity between logarithm of specific resistance and pressure in the lower range below $15,000$, the curve being concave down toward the pressure axis. At $15,000$ there is a reversal of direction of curvature with an abruptness giving a definite cusp when the plot is made on a suitable scale. Although logarithm of specific resistance is not linear for this specimen below $15,000$, the resistance itself is linear. In Figure 4 the experimental points are plotted on a different scale for this specimen. Two runs were made, at slightly different temperatures (21.9° and 22.3°), the second run with points more closely spaced up to $20,000$, in order to exhibit more definitely the break in direction. The sharpness and definiteness of this break in direction near $15,000$ becomes increasingly obscured in the other specimens with increasing degree of impurity.

In theoretical speculations as to the significance of the accelerated rise of resistance above $15,000$ it is to be remembered that the rise does not increase indefinitely but as shown by the previous

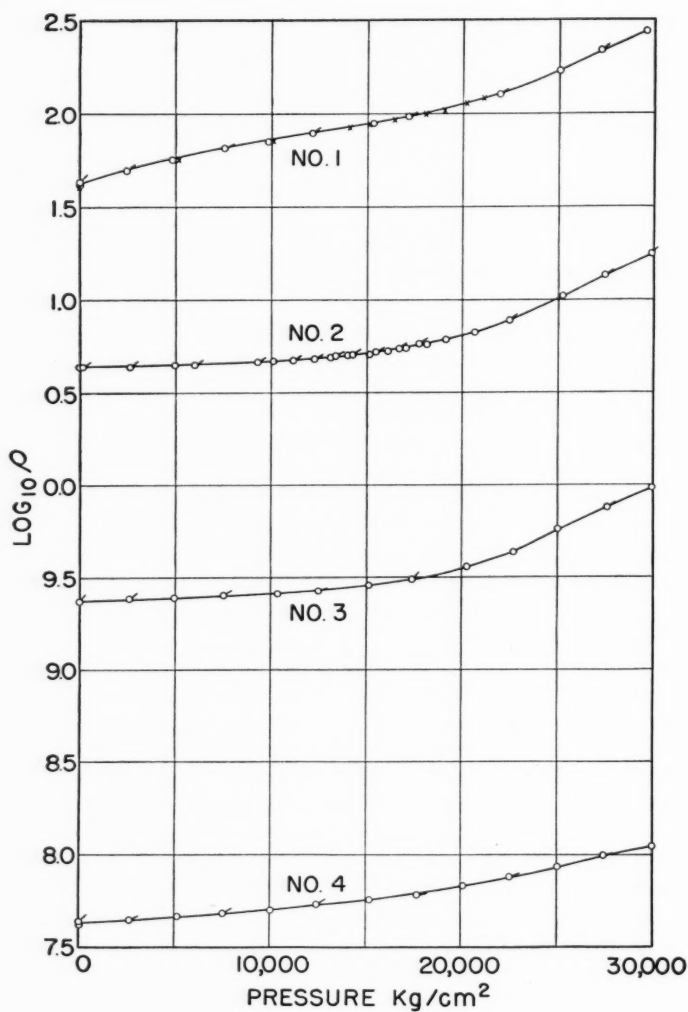


Figure 3. The logarithm of the specific resistance at room temperature of four specimens of n-type germanium as a function of pressure to 30,000 kg/cm^2 .

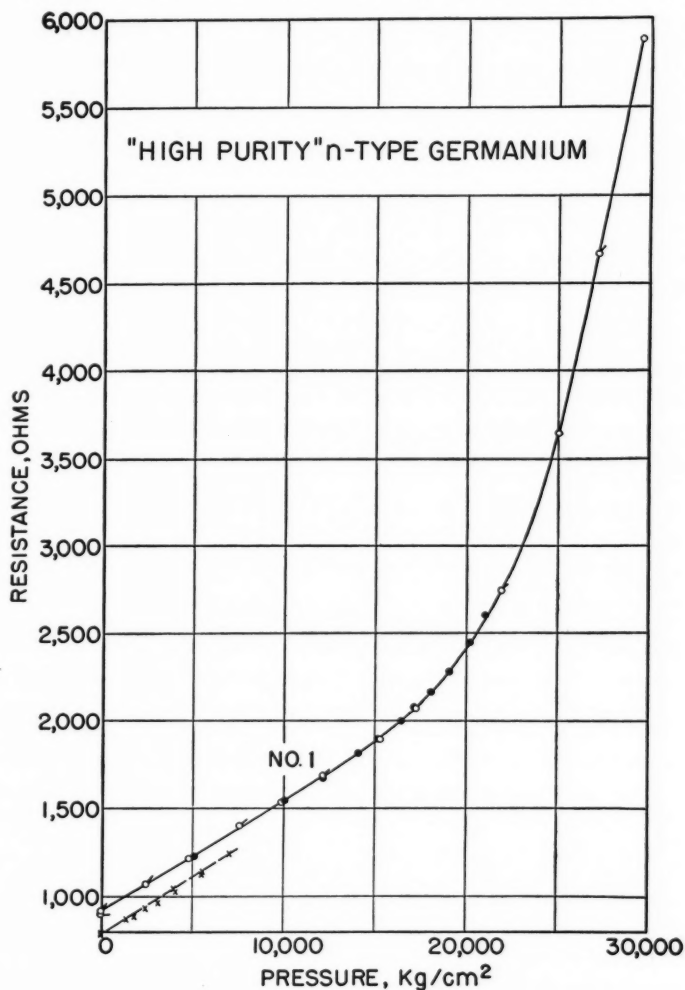


Figure 4. The actual resistance of the specimen of highest purity as a function of pressure to 30,000 kg/cm² (open and solid circles). The points indicated by crosses were obtained with the nitrogen apparatus of the first part of this paper. The initial slopes of the two sets of measurements are the same; the absolute value of resistance is not significant.

measurements to 100,000 is terminated by some sort of a catastrophe near 45,000, with rapid decrease of resistance beyond.

Previous measurements on the resistance to 30,000 at room temperature of p-type germanium of specific resistances 1.6 and 3.33 have given a nearly linear decrease of resistance over the entire range at the rate of -2.0 per cent per $10,000 \text{ kg/cm}^2$ for the first specimen and -2.2 per cent for the second specimen. In the present work similar measurements were made on two specimens of initial specific resistances at 24° of 0.866 and 0.932. These two specimens were cut from the same crystal; the variation of resistance is evidence of slight inhomogeneity in the material. Both of these specimens decreased in resistance under pressure at a rate approximately linear with pressure. The total decrease under 30,000 of the first specimen was 6.29 per cent and of the second 5.91 per cent, thus agreeing essentially with the previous results. To a second approximation the decrease is not linear with pressure, but decreases in rate at the higher pressures. Thus the average coefficient over the first $15,000 \text{ kg/cm}^2$ of the second specimen above was 2.16 per cent per $10,000 \text{ kg/cm}^2$ against an average coefficient over 30,000 of 1.97 per cent.

The heavily doped specimen of initial specific resistance 0.000794 was also measured. This *increases* in resistance linearly over the entire range within errors of measurement at a rate of 1.02 per cent per $10,000 \text{ kg/cm}^2$. The sign for the heavily doped p-type is thus the same as for the heavily doped n-type but numerically it is much less, being only one twentieth of the initial rate of the n-type.

I am much indebted to Mr. Charles Chase for assistance in making these experiments.

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INTRODUCTION

In the following are collected a number of not very closely related measurements of the effect of pressure on the electrical resistance of metals, none of them extensive enough to justify publication separately, but all of them containing new information and presumably worth recording somewhere. There are in the first place measurements of the effect of pressure at higher temperatures than I have hitherto employed. For these measurements an old apparatus¹ designed for use at liquid oxygen temperature was restored and adapted to use up to 200°C, my previous limit having been 95°C. This restored apparatus was principally used for measurements on various specimens of germanium into the intrinsic range of temperature; these results are being published in a separate paper. Advantage is here taken of the availability of the apparatus to check to more than double the previous temperature range my former generalization that the pressure coefficient of resistance is approximately independent of temperature. This

check was made for only a few metals, choosing those for which it was anticipated that any effects might be largest. The pressure range of this work to 200° was only $7,000 \text{ kg/cm}^2$.

In the second place, opportunity was taken of the availability of highly purified specimens of tellurium, which I owe to the kindness of Professor Harry H. Hall, to explore more extensively than hitherto the resistance of this substance. Measurements are here presented both in the $7,000$ range to 200° and in the $30,000$ range at room temperature. These measurements have their bearing on the question of semi-conductors, which are at present attracting so much interest.

Finally, there are several metals available in greater purity than before or else not formerly available. Uranium in the form of wire of presumably greater purity than previously available was supplied by the Los Alamos Laboratory of the AEC. This was measured to $30,000$ at room temperature. Hafnium is now available in this country; previous measurements to $12,000$ are here extended to $30,000$ and to $100,000$ at room temperature. Metallic rhenium is available in the form of powder, but not in massive form. By shearing at $100,000 \text{ kg/cm}^2$ it is converted into a form sufficiently homogeneous to make it seem worth while to measure the effect of $100,000 \text{ kg/cm}^2$ on the electrical resistance. Specimens of rhenium sufficiently large for measurement with other sorts of apparatus were not produced by the shearing method. Finally, pure gadolinium in massive form was available from Dr. Spedding's laboratory of the AEC at Ames, Iowa, and measurements are here given at room temperature in the $30,000$ and $100,000$ ranges.

In addition to the measurements on electrical resistance, measurements were made incidentally on the shearing strength of a few of these materials up to mean pressures of $100,000 \text{ kg/cm}^2$, and also on the cubic compressibility of gadolinium.

THE RESULTS

In general comment on the measurements to 200°C and $7,000 \text{ kg/cm}^2$, the apparatus and method have been sufficiently described in the preceding paper on germanium.² Slight and obvious enough changes were demanded in the electric circuits in order to deal

with the lower resistance of the metals measured here as compared with germanium. Five metals were so measured: tin, lead, cadmium, aluminum and copper. It is probably to be expected that any enhancement of the previous very small effect of pressure on temperature coefficient of resistance (or of temperature on pressure coefficient) due to the present more extensive temperature range will be greatest on those metals with the lowest melting points, simply because the general loosening up of the structure by temperature is greatest for the low melting metals. The effect would therefore be expected to be greatest for tin and least for copper. I think it is also to be anticipated that the effect, such as it is, will be positive, that is, an arithmetic increase of pressure coefficient at higher temperatures.

Tin. This was "Kahlbaum" grade, from my stock of many years ago. It was extruded to wire 0.010 inch in diameter, and wound bare in the grooves of a pipestone spool. Measurements were made at three temperatures: 0°, 100.1° and 203.8°. The relation between pressure and resistance was very approximately linear, but with perceptible departure in the normal direction, that is, a decreasing coefficient at higher pressure. No attempt was made to evaluate the second degree term. The average pressure coefficients to 7,000 kg/cm² were -9.47×10^{-6} , -9.64×10^{-6} , and -10.13×10^{-6} respectively, at the three temperatures. This behavior is thus in line with that expected. Furthermore, the effect becomes accelerated at the higher temperatures, the extra hundred degrees of the present measurements magnifying the comparatively small effect in the former temperature range. The average temperature coefficient at atmospheric pressure was 0.00435 between 0° and 203.8° and 0.00440 between 0° and 100.1°. It is more usual for the temperature coefficient to increase with rising temperature.

It is to be mentioned that tin is non-cubic (tetragonal), and that strictly a single crystal should have been used rather than extruded wire. However, it is known that the departures from isotropy of tin are small, both with respect to resistance and compressibility, so that complications due to the extruded form are probably unimportant.

Lead. The material was of 99.9999 per cent purity, obtained a number of years ago from the Federated Metals Corporation, and used in many of my previous measurements. For the present

measurements it was extruded cold to wire of 0.010 inch diameter and wound non-inductively on a pipestone spool. Measurements were made at 0° and 204.0° . The average temperature coefficient of resistance at atmospheric pressure over this range was 0.00427. The relation between pressure and resistance departs notably from linearity in the normal direction, but no attempt was made to get the exact deviation from linearity. The average pressure coefficient to 7,000 kg/cm² was -1.286×10^{-5} at 0° and -1.360×10^{-5} at 204.0° . The change with temperature of the pressure coefficient is thus in the expected direction. Previous measurements³ at 30° and 75° had given an increase of mean coefficient to 5,000 kg/cm² of 0.73 per cent for the temperature increment of 45° , against a present increment of 5.7 per cent for a temperature increment of 204° . The temperature effect on pressure coefficient thus increases more rapidly than linearly with increasing temperature, again in line with expectations. The increment 5.7 per cent is to be compared with an increment of 7.0 per cent for tin for the same temperature range. Tin, the lower melting metal, thus has the greater increment, again in line with expectations.

Cadmium. This was spectroscopically pure material from the New Jersey Zinc Company, extruded to wire of 0.010 inch diameter. Runs were made at 0° and 203.9° . At 0° the mean coefficient to 7,000 kg/cm² was -8.31×10^{-6} , with slight deviation from linearity in the normal direction. At 203.9° there was an upward jump in resistance of 0.6 per cent between 2,400 and 4,000 kg/cm². It seems probable that this jump is connected with the transition previously found⁴ in cadmium at lower temperatures. This transition is somewhat obscure and has been found up to now only in single crystal material. The initial coefficient in the present measurements at 203.9° before the transition was -8.81×10^{-6} ; after the transition the average coefficient to 7,000 was -9.81×10^{-6} . The transition did not run in the reverse direction on releasing pressure to atmospheric at 203.9° , neither did it run on lowering temperature again to 0° at atmospheric pressure, but there was a permanent increase of resistance at 0° of 2.4 per cent. The mean temperature coefficient of resistance between 0° and 203.9° at atmospheric pressure was 0.00462 before the transition and 0.00449 after it.

No clean-cut interpretation of the results is obvious. It is known

that the transition is such that the original crystal orientation is not recovered even when the reverse transition runs. The meaning of the results is further obscured by the fact that cadmium is not cubic and the differences in different directions in the crystal are important. The results before the transition do indicate, however, an effect of temperature on the pressure coefficient in the expected direction.

Aluminum. This was the identical specimen as previously measured¹ in the same apparatus at liquid oxygen temperature. Runs to 7,000 kg/cm² were made at 0° and 203.9°. The average temperature coefficient over this range at atmospheric pressure was 0.00460. The relation between pressure and resistance was linear within the error of measurement. At 0° the mean pressure coefficient to 7,000 was -4.26×10^{-6} and at 203.9° -3.90×10^{-6} . The temperature effect is thus not in the expected direction. The direction now found is, however, consistent with the variation previously found in the range below 0° down to -182°. Aluminum was unique among the fifteen metals previously measured in this range in the magnitude of the temperature effect.

Copper. Commercial copper wire was used, 0.003 inch in diameter, teflon covered. Runs were made at 0° and 204.2°. The mean temperature coefficient of resistance at atmospheric pressure in this temperature range was 0.00433. The relation between pressure and resistance was sensibly linear in the range to 7,000, and the identical mean coefficient was found for both temperatures, -1.89×10^{-6} . This is in line with expectations that the temperature effect is smaller for the higher melting metals.

Tellurium. Extensive measurements have been made on highly purified tellurium by H. H. Hall⁵ up to 10,000 psi and at temperatures between 0° and 90°C. Professor Hall most kindly provided me with specimens of tellurium for further investigation. It was in the first place of interest to find whether there is an important change of behavior over my somewhat wider range with the nitrogen apparatus, that is, up to 7,000 kg/cm² (100,000 psi) and 200° C. Measurements were made on one specimen in the nitrogen apparatus. The specific resistance, ρ , of this specimen at atmospheric pressure at dry ice temperature (-78°) was 3.73 ohm cm. This corresponds to one atom of acceptor impurity per 10^7 atoms of tellurium. The measurements disclosed nothing novel, and the

numerical results were in line with what was to be expected from the measurements of Hall. Logarithm of resistance against pressure is concave upward (diminishing slope at higher pressures) and the average slope is less at the higher temperature. At 0° $\log_{10} \rho_0 / \rho_{7000} = 0.958$. The value which $\log_{10} \rho_0 / \rho_{7000}$ would have had if the relation had been maintained linear over the entire pressure range was 1.201. This corresponds to an initial rate of decrease of resistance of 2.82 per cent for 1,000 psi, which is only slightly higher than the value of Hall for a specimen of not quite as high purity. At 203.9° the corresponding values for $\log_{10} \rho_0 / \rho_{7000}$ were 0.796 and 0.910. The latter is equivalent to an initial rate of decrease of 2.13 per cent per 1,000 psi.

Advantage was taken of the possibility of obtaining material of known and high purity to examine further the effects of considerably higher pressures at room temperature. In particular, it was desired to explain the much smaller effect of pressure found in my most recent measurements to 100,000 as compared with my previous measurements to 30,000. Two possible explanations offered themselves. One was that the shearing strains incident to the transmission of pressure by AgCl in the measurements to 100,000 produce large changes of resistance. A second possibility, suggested by Professor Hall, was that during the extrusion in preparing the material for measurement to 100,000 sufficient impurity, presumably iron, had been introduced to importantly depress the pressure coefficient, it having been Professor Hall's experience that comparatively small amounts of impurity do this. To settle this question it was proposed to make measurements to 30,000 on the highly purified material of Professor Hall, then to extrude these through steel dies and recast them to the original shape and re-determine the effect of pressure.

Measurements were carried out on three different specimens. I first measured the resistance at room temperature to 30,000 kg/cm^2 . I then melted each specimen in high vacuum in a pyrex tube of $\frac{1}{4}$ inch diameter. It was solidified in the tube, removed to a steel die, and extruded to $\frac{1}{8}$ inch diameter at approximately 350°C . This extrusion left the specimens very rough, with many fissures. Professor Hall then "melted in helium in pyrex which had been cleaned in hot chromic acid cleaning solution and rinsed in distilled water until the electrical conductivity of the wash

water was less than one part per million referred to NaCl." After melting, two of the specimens were "quenched" by removing from the hot zone of the furnace into a region at room temperature. The third was recrystallized by raising the furnace heater slowly

TABLE I
SUMMARY OF RESULTS FOR TELLURIUM

Specimen	Specific Resistance at -78°		$R_0/R_{30,000}$		Remarks
	Original	After Extrusion and Melting	Original	After Extrusion	
1	1.7 ohm cm	0.59	195	537	quenched
			360		
2	2.5	0.038	209	39	quenched
			347	76	
3	4.2	0.41	145	288	slowly cooled
			282		
single crystal	0.5		400		two orientations
			600		

so that the sample was progressively cooled, starting at one end, in about an hour. This latter treatment has been found to be especially effective in removing impurity. The three specimens thus prepared were then remeasured by me to 30,000 at room temperature. The results are given in Table I. It will be seen that two figures are given in several instances for the ratio $R_0/R_{30,000}$. There are two reasons for the uncertainty thus indicated. On release of pressure there may be a permanent increase of resistance. The two figures (39 and 76) given for specimen No. 2 after treatment are the values obtained using the initial and the final values of R_0 . In addition, during the first series of measurements, an uncertainty was introduced by a loose electrical connection which was not discovered until the termination of those measurements. The two figures given in the column of original measurements include both any effect from a possible permanent change of zero and the maximum and minimum possible effects of the loose connection.

It will be seen from Table I that the permanent decrease of resistance after extrusion and presumable introduction of iron as

an impurity is much larger for specimen No. 2 than for the two others. It is also for specimen No. 2 that the decrease of pressure effect is large and unmistakable, as suggested by Professor Hall. For the other two specimens, however, for which the diminution of resistance was less, the pressure effect is actually increased. It would appear therefore that in the range of comparatively slight impurity there are other effects on the pressure coefficient more important than impurity. These effects are, furthermore, capricious, as emphasized by a comparison of the data for my former single crystal material,⁷ included in the table, with the results for the present material. It appears probable that two related factors are primarily responsible for this capriciousness, both connected with the failure of the specimens to be single crystals. In the first place, the resistance is different in different directions in the crystal, being greater by 75 per cent in one direction than another, with an 8 per cent variation of pressure coefficient in these directions. This means that specific resistance by itself is not an adequate parameter to completely describe the nature of the material. In the second place, the cubic compressibility varies with direction in the crystal by an abnormally large amount for tellurium, there being differences of sign in different directions. This means that when a multi-crystalline specimen is exposed to hydrostatic pressure shearing stresses are developed, which may conceivably lead to fracture for high enough pressures, particularly in this unusually brittle material. This is consistent with my observation that always after exposure to 30,000 kg/cm² a number of cracks appeared in Professor Hall's specimens, although there were none in my single crystal material. Professor Hall's pressure range was not sufficient to result in cracking in his own experiments.

Several conclusions may be tentatively drawn. My unexpectedly small pressure effect in the experiments to 100,000 kg/cm² may well be a combination of effects of impurity introduced by the extrusion process and the shearing stresses incident to non-hydrostatic stress. For tellurium of purity greater than say 0.5 ohm cm at -78° the effect of impurity on pressure coefficient is probably less important than that of non-isotropy and failure of uniaxiality. For reproducible and completely significant results on high purity tellurium it would appear essential that the material be uniaxial and that the crystal orientation be known.

Uranium. This I owe to the courtesy of the Brookhaven National Laboratory. The point in repeating former measurements⁸ to 12,000 kg/cm² was that this new material would presumably be purer. It was supplied in the form of "wire . . . 6 inches long and 0.020 inch in diameter, weighing 0.648 gram, of normal uranium isotopic constituency. It is approximately 99.9 per cent pure, and can be handled as unclassified material." Four leads were attached by spot welding, and measurements made to 30,000 kg/cm² in my regular way. Results were normal in every respect; the numerical values are given in Table II.

TABLE II

EFFECT OF PRESSURE ON RESISTANCE OF URANIUM

Pressure kg/cm ²	$-\frac{1}{p} \frac{\Delta R}{R_0}$
0	4.880×10^{-6}
5,000	4.71
10,000	4.56
15,000	4.436
20,000	4.317
25,000	4.206
30,000	4.104

Former measurements⁸ had given a linear drop of resistance with pressure over the range to 12,000 kg/cm² with a mean coefficient -4.36×10^{-6} . The pressure effect on the present specimen is thus somewhat larger than on the former; the difference is in the direction to be expected from greater purity in the present specimen. The mean temperature coefficient of resistance at atmospheric pressure between 0° and 100° of the present specimen is 0.00248 against a former value 0.00230. The difference is not large, but again in the direction of greater purity for the present specimen. It would appear probable that the temperature coefficient of this metal in the pure state is significantly lower than the traditional value for a pure metal, $1/T$ or 0.00367.

In the normal course of events I would also have measured the resistance of this new material with my new technique⁶ to 100,000 kg/cm². This, however, would have involved mutilation of the

specimen, and since this would have involved considerable red tape to obtain the necessary permission and presumably would have given results not greatly different from those formerly found, I chose the easiest way, and returned the specimen as received to Brookhaven, as requested.

Rhenium. This was obtained in the form of powder from Eimer and Amend via the Brookhaven National Laboratory. Apparently there are no measurements whatever on this material in massive metallic form. An exploratory examination for possible new polymorphic forms at high pressure was made by the shearing technique⁹ with a new carboloy apparatus to 100,000 kg/cm². The shearing measurements were perfectly smooth over the entire range, indicating no polymorphic transitions. The general magnitude of the plastic flow strength was approximately 20 per cent greater than that of copper, and the manner of variation with pressure was about the same as for copper. The product of the shearing was a coherent disc of metallic appearance of sufficient mechanical strength to invite a determination of its properties, in view of our complete ignorance of any such. The only property readily measurable on such small specimens was the electrical resistance to 100,000 kg/cm², for which the dimensions were well adapted. Runs were accordingly made by the regular technique⁶ on two specimens to 100,000. Below 20,000 the two runs differed considerably, as is usual, but above 20,000 the agreement of the two runs was rather good, one giving the value 0.712 for the ratio $R_{100,000}/R_{20,000}$ and the other 0.701. The average for the two runs is given in Table III. The pressure effect on resistance is of the general order of that characteristic of the softer metals, and is not far from that of tin.

A very rough value for the specific resistance at atmospheric pressure at room temperature is 6×10^{-4} ohm cm; doubtless this value is too high. The most secure of the present results with this new material would seem to be that there is no discontinuity up to 100,000 kg/cm² at room temperature, a result given by both shearing and resistance measurements.

Hafnium. The electrical resistance and compressibility of hafnium have been previously measured¹⁰ up to 12,000 kg/cm² in 1928. The material was loaned by the Research Laboratory of the Philips Lamp Works in Eindhoven, Holland, and was returned to them

after the measurements. Zirconium, which is similar chemically to hafnium, has recently been found¹¹ to have a transition in the neighborhood of 80,000 kg/cm². It therefore appeared of interest to extend the measurements on hafnium to higher pressures. Some difficulty was experienced in locating suitable material. The Eindhoven Laboratory had lost theirs during the German occupation. On running down a number of references in the recent literature to properties of hafnium no suitable material was uncovered.

TABLE III

EFFECT OF PRESSURE ON RESISTANCE OF RHENIUM

Pressure kg/cm ²	$R_p/R_{20,000}$
10,000	1.140
20,000	1.000
40,000	.856
60,000	.787
80,000	.742
100,000	.706

Finally, through the Foote Mineral Company, I was put in contact with work by the U. S. Air Force on this material, who were interested in it from the point of view of jet engines. A small quantity of pure massive material was kindly made available for my measurements by the Wright Air Development Center at Dayton, Ohio. Various physical properties of this material have been described in print.¹² Of the several specimens of hafnium studied in that paper only one, bar No. 778, "as deposited iodide crystal bar" had high presumptive purity, as indicated by the agreement of its physical properties with previously published values. This purity was stated, without analysis, to be indefinitely better than 99 per cent. My specimen was a small block cut with a saw from bar 778. For my measurements two small slivers were cut from the block and rolled in four passes to a thickness of 0.007 inch from an initial thickness of the order of 0.040 inch. One of these pieces was rolled without annealing, whereas the other was annealed at every pass in quartz in vacuum at a temperature of approximately 1050°C. The rolled strips were finally reduced by hand filing to a thickness of 0.002 inch.

Two sets of measurements were made: of resistance at room temperature to 30,000 kg/cm² with true liquid as the transmitting medium, and of resistance at room temperature to 100,000 with AgCl transmitting. For the 30,000 measurements dumbbell shaped pieces were cut from the rolled strip, the isthmus of the dumbbell being 0.9 cm long and 0.05 cm wide, and two terminals were attached by spot welding to each end of the dumbbell. Measurements at 30,000 gave smooth regular variation of resistance. Resistance decreases under pressure, with normal curvature. The coefficient is small compared with that of most metals. Within the limit of error, which was not anywhere greater than one part in 300 on the total change of resistance, decrease of resistance can be represented by a second degree formula in the pressure. This means that $\frac{1}{p} \frac{\Delta R}{R_0}$ is linear in pressure. For the unannealed specimen the value of $\frac{1}{p} \frac{\Delta R}{R_0}$ ran from -8.78×10^{-7} at atmospheric pressure to -7.06×10^{-7} at 30,000 kg/cm². For the annealed specimen the corresponding values were -9.31×10^{-7} and -7.54×10^{-7} . The latter is to be preferred as more truly representative of the metal. The mean temperature coefficient of resistance at atmospheric pressure between 0° and 100° was 0.00419, and the specific resistance at 0° 29.7×10^{-6} ohm cm. The latter figure is only rough because of uncertainty in estimating the correct effective length of the specimen; it is to be compared with the value 32.0×10^{-6} for the same material by Adenstedt. My previous measurements¹⁰ to 12,000 kg/cm² on hafnium had given at 30° a linear relation between pressure and resistance with a mean coefficient of 10.0×10^{-7} . The former specific resistance at 0° was 31.9×10^{-6} and the mean temperature coefficient between 0° and 100° 0.00398.

Measurements of resistance to 100,000 were made by the regular technique on two specimens from the same annealed strip as used to 30,000. Both runs to 100,000 gave smooth results, with no suggestion of any transition, such as had been shown by zirconium. In terms of the resistance at 20,000 as fiducial the changes in proportional resistance at 100,000 given by the two runs were 0.0338 and 0.0322, which is rather good agreement for material with as small an absolute effect as this. The two runs were averaged, and

the decrement of proportional resistance reduced uniformly by 21 per cent over the entire range in order to secure agreement with the previous measurements in the range to 30,000. The final results for the proportional change of resistance are given in Table IV. The readings below 10,000 were taken from the 30,000 runs. *Gadolinium*. The material was in the form of a massive hunk weighing about 3 grams prepared by the AEC at Ames, Iowa, under the direction of Dr. Frank Spedding. This is the first time

TABLE IV

EFFECT OF PRESSURE ON RESISTANCE OF HAFNIUM

Pressure kg/cm ²	$-\frac{\Delta R}{R_0}$
0	.0000
10,000	.0087
20,000	.0163
30,000	.0227
40,000	.0279
50,000	.0316
60,000	.0348
70,000	.0374
80,000	.0393
90,000	.0408
100,000	.0419

that this material has been available for my measurements. Four different sorts of pressure measurement were made: shearing to 100,000 kg/cm², electrical resistance to 100,000, electrical resistance to 30,000, and cubic compressibility to 40,000. Four metals in the rare earth group have previously been measured⁶ to high pressures: cerium, lanthanum, praseodymium, and neodymium. All have shown anomalies, but no two alike. The question of major interest here was whether gadolinium would also be anomalous, and if so, what is the nature of the anomaly. The results may be anticipated to say that an anomaly was found, different from any of the others.

The measurements of resistance to 30,000 at room temperature have the greatest relative accuracy, and they will be described first. The specimens were prepared in much the same way as hafnium. A small sliver was cut from the original hunk with a

cold chisel, rolled in four stages from 0.025 to 0.004 inch thick, with annealing in quartz at high vacuum to approximately 1050°C after each rolling. From the strip thus obtained a dumbbell shaped piece was cut and two terminals of fine platinum attached by spot welding to each of the two broad tabs of the dumbbell. It was found incidentally that platinum rapidly alloys with gadolinium at high temperatures. Unlike the other four rare earth metals, gadolinium appears to be stable in air at room temperature. It was shipped to me freely exposed to air, and during my preliminary manipulations no precautions were taken to protect it from the air, as seemed unnecessary because of the appearance. Contrasted with its inertness in air is violent chemical activity in contact with "Eliot's" soldering fluid, a neutral flux often used where freedom from subsequent corrosion of the soldered connection is deemed essential. In contact with this fluid gadolinium bubbles violently and rapidly dissolves. The nature of the chemical attack was not investigated further; it is known that Eliot's fluid contains a large proportion of alcohol.

When exposed to 30,000 gadolinium exhibits an instability in resistance beginning at approximately 20,000. Below this, resistance is steady under constant pressure. Above 20,000 resistance at constant pressure drifts rapidly downward. This drift occurs in the entire region between 20,000 and 25,000. If there is any tendency to asymptotic cessation of drift at any pressure in this range it was too slow to be found in the course of ordinary manipulation. Between 25,000 and 30,000 readings are approximately constant at fixed pressure, but the slope of the curve of resistance against pressure is much greater than at lower pressures. On release of pressure reversal of drift does not occur, but readings are constant all the way back to atmospheric pressure, where the initial resistance is diminished by approximately 7 per cent. At atmospheric pressure there appears to be a very slow drift of resistance back toward the initial value; on standing three days at atmospheric pressure there was a one per cent recovery of resistance. Repetition of the pressure run now gave approximately the same curve as on the first release of pressure, but with hysteresis in the one per cent range corresponding to an internal change only one seventh of that at first. The virgin behavior of the material may be completely restored by an annealing after the pressure run

to 1050°C. How much lower a temperature would have sufficed was not investigated.

The averages of the two runs on freshly annealed material are given in Table V. Up to 20,000 the two runs agreed within one per cent on the change. The agreement was not so good during the transition and on release of pressure, the relative change of resistance for one run being 5 per cent greater than for the other (0.2049 against 0.1935). The permanent changes of zero after release of pressure were 0.0680 and 0.0767. It will be noticed that

TABLE V

EFFECT OF PRESSURE TO 30,000 kg/cm² ON
RESISTANCE OF GADOLINIUM

Pressure kg/cm ²	- $\Delta R/R_0$ Increasing Pressure	Decreasing Pressure
0	.0000	.0723
10,000	.0459	.1317
20,000	.0885	.1709
25,000	.1711	.1862
30,000	.1992	

the departure from linearity is much greater on release of pressure, after the transition has run, than on the first application of pressure.

The temperature coefficient of resistance at atmospheric pressure between 0° and room temperature of the freshly annealed material was 0.00176, and of the material previously exposed to 30,000 0.000908 (identical values for the two specimens). Again a temperature coefficient is obtained for a presumably pure rare earth metal materially less than the traditional 1/T.

The specific resistance at 0° of the annealed material was 140.5×10^{-6} ohm cm, and of the pressure exposed material 134.5×10^{-6} .

Measurements of resistance to 100,000 kg/cm² were made on two specimens cut from the same strips as had supplied the specimens for 30,000. Both of these runs showed the same effect between 20,000 and 25,000 as had the 30,000 series. This disturbance makes it impossible to estimate the reduction factor that would secure agreement between the 30,000 and the 100,000

series, so that the present series has had to be accepted at its face value between 30,000 and 100,000. The decrements of proportional resistance at 100,000, in terms of the resistance at 30,000 as unity, were 0.1904 and 0.2100 for the two runs. These were simply averaged for the final results, which are given in Table VI. In this table the values to 30,000 are copied from Table V. It will

TABLE VI
EFFECT OF PRESSURE TO 100,000 kg/cm² ON
RESISTANCE OF GADOLINIUM

Pressure kg/cm ²	R/R ₀
0	1.0000
10,000	.9541
20,000	.9115
30,000	.8008
40,000	.7637
50,000	.7322
60,000	.7056
70,000	.6844
80,000	.6668
90,000	.6523
100,000	.6405

be seen that the resistance above 30,000 decreases smoothly with pressure; there is no evidence of any further transition. This was confirmed by the shearing measurements to 100,000, which will be described in fuller detail in another paper. The transition at 25,000, or whatever it is, is reflected in the shearing measurements by a point of inflection with reversal of curvature from concave down to concave up. This abnormal upward concavity continues over the entire range to 100,000, but there is no new incident to indicate any further internal change. The absolute magnitude of the shearing strength to 100,000 is of the order of half that of copper.

Since the compressibility of gadolinium appears to have never been measured, opportunity was taken to measure it to 40,000 in my conventional apparatus,¹³ and the results are given here for the sake of completeness, although not related to electrical resistance. Since gadolinium is somewhat stiff mechanically, that

method was employed in which the gadolinium is surrounded by a sheath of indium in order to transmit pressure uniformly. The compressibility of the indium was eliminated by making a new blank run with iron, the immediate results of the measurements being the differential compressibility between gadolinium and iron. Two set-ups were made on two different specimens; the volume decrement at 40,000 of the two sets differed by 0.37 per cent of themselves. Two complete runs were made with each set-up, embracing two excursions with increasing pressure and two with decreasing. Of these four excursions the three last gave the compressions of the material as modified by the quasi-permanent transition between 20,000 and 25,000 kg/cm². The two initial excursions gave a distinct break in the volume between 20,000 and 25,000 corresponding to the break in resistance. This break, which of course was in the direction of a decrease of volume, had the numerical magnitude $\Delta V/V_0 = -0.00432$. There was no perceptible break in the direction of the tangent on the two sides of the break; that is, the transition runs with no measurable change in compressibility. The final values are given in Table VII.

TABLE VII

COMPRESSION OF GADOLINIUM TO 40,000 kg/cm²

Pressure kg/cm ²	$\Delta V/V_0$
0	.0000
5,000	.0125
10,000	.0242
15,000	.0351
20,000	.0452
25,000	.0545
30,000	.0632
35,000	.0712
40,000	.0785

These values are for the material as altered by a preliminary application of 25,000 or more. In order to obtain the volume decrements of the freshly annealed material it is sufficient to add to the above values 0.0043 from 25,000 on (inclusive).

The compression of gadolinium is distinctly less than that of the four other rare earth metals previously measured.¹⁴ It ap-

proaches most closely to neodymium, for which the volume decrement under 40,000 is 0.0955 as compared with 0.0785 above for gadolinium.

In the course of the compressibility measurements the density at room temperature was incidentally determined. This was 7.964 at 26° for material previously exposed to pressure.

It will be interesting to measure the effects of high pressure on other members of the rare earth series of metals as soon as they become available. The rare earth metals as a class are characterized by incomplete inner electron shells. Under high pressure these shells may be expected to become occupied by electron transfer from outer shells, so that we have here perhaps the most favorable opportunity of studying pressure induced electronic rearrangement within the atom, a phenomenon which must become increasingly important for all atoms at higher pressures.

It is a pleasure to acknowledge the assistance of Mr. Charles Chase with these measurements.

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THE EFFECT OF PRESSURE ON SEVERAL PROPERTIES OF THE ALLOYS OF BISMUTH-TIN AND OF BISMUTH-CADMIUM

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INTRODUCTION

Comparatively little is known of the effect of pressure on the properties of alloys. The results presented here are the beginning of what is hoped will become a systematic program of investigation. Various considerations present themselves in choosing the alloys for first investigation. One might, for example, expect interesting results with those alloys for which one or the other of the two pure components is already known to have interesting pressure effects. From this point of view bismuth, with its known abnormal properties under pressure and its various polymorphic transitions, is perhaps the most natural first candidate for one of the components. An additional consideration is the ease of handling of many of the alloys of bismuth — the melting point is low, chemical activity in the air is not serious, and most of the alloys are not so brittle as to make it difficult to get them into suitable geometrical shape for measurement.

In the following, results are presented for the two series, bismuth-tin and bismuth-cadmium. Bismuth-tin is known to form a simple eutectic series at atmospheric pressure.¹ At the two ends of the composition range solid solutions are formed up to definite composition limits; at intermediate compositions the system breaks up into a mechanical mixture of the two limiting compositions. Bismuth-cadmium, on the other hand, is not known to exhibit mutual solubility at all,² and at all compositions the system breaks into a mechanical mixture of the pure components. It is to be expected therefore that the pressure effects will be simpler on the bismuth-cadmium than on the bismuth-tin series. This proved to be the case. The results for the bismuth-tin series were further complicated by the unexpected entry of an intermetallic compound of bismuth and tin requiring 20,000 kg/cm² or more for its formation. As a consequence of this complication by far the larger amount of space in this paper is devoted to the bismuth-tin series.

The measurements presented in the following were all made by standard techniques which I have applied in the past to various pure metals.³ The measurements include: electrical resistance to 30,000 kg/cm², pressure transmitted by a true liquid; electrical resistance to 100,000 kg/cm², pressure transmitted by AgCl; cubic compressibility to 40,000 kg/cm²; and shearing strength to

100,000 kg/cm². In addition, the following were measured at atmospheric pressure: density, specific resistance, and temperature coefficient of resistance.

THE BISMUTH-TIN SERIES

It will probably increase the perspicuity of the presentation to first briefly describe the nature of the novel effects found under pressure. Apparently the intermetallic compound BiSn becomes possible under pressure. This compound itself undergoes a polymorphic transition at 20,000 kg/cm², and it is only the high pressure modification of the compound which can be formed by direct transformation out of the previously known eutectic mixtures stable at atmospheric pressure. This means that on first increasing pressure on the virgin eutectic system nothing unusual happens until 20,000 or more is reached, when there is an irreversible transformation to the high pressure modification of the compound. The system after the transformation consists of the high pressure modification of the compound mixed in various proportions with the limiting solid solutions, depending on the gross composition. Further increase of pressure encounters the polymorphic transitions of bismuth, which occur in the general neighborhood of 25,000 and 27,000 kg/cm² for pure bismuth and which occur at very nearly the same pressures for dilute solutions of tin in bismuth. On release of pressure the transitions in which bismuth plays the dominating role are first encountered, and then, at a pressure in the neighborhood of 15,000 kg/cm², the reversible transition of the compound to its low pressure form. Release of pressure to atmospheric now gives a system composed partly of the original constituents and partly of the low pressure modification of the compound. A second increase of pressure first encounters the reversible transition of the compound near 15,000 with the other polymorphic transitions at higher pressures. A second release of pressure approximately reproduces the behavior on the first release. The low pressure modification of the compound is not indefinitely stable at atmospheric pressure at room temperature, but slowly reverts. The speed of reversion is much increased at elevated temperatures and may be practically suppressed at dry ice temperature. In the following a few measurements have been made of the speed of reversion.

The alloys were prepared by melting together in pyrex in vacuum weighed amounts of the pure components. The tin was old Kahlbaum "K" stock, and the bismuth was from my stock of specially purified material, purified first electrolytically and then by crystallization into single crystal form. The alloys were prepared in batches of approximately two grams. The composition was not checked after formation, but a check on loss of metal during the alloying was obtained by weighing the nugget after formation. Loss of material of as much as 0.001 gram was not common. The molten metals were violently agitated together and rapidly solidified in order to give a homogeneous product. The resulting nugget, after breaking away the glass and weighing, was scraped bright and divided into two approximately one gram lots. One of these was extruded to a wire of approximately 0.020 inch diameter for the resistance measurements to 30,000. For extrusion, temperature was raised to slightly less than the eutectic temperature, 140° . The extruded wire was of the order of one meter in length. Homogeneity of composition over the wire was checked in several instances by resistance measurements on specimens cut from the two ends. No examples of measurable inhomogeneity were found. The second one gram piece was used for the compressibility measurements to 40,000. Density determinations were made on this piece, usually both before and after exposure to pressure. Density was determined by weighing in air and in CCl_4 . This fluid proved to be very much superior to water for this purpose; it is 50 per cent denser than water, the surface tension is low, it dissolves any surface film of grease on the specimen, and air bubbles do not cling to the specimen. Some seventeen different compositions were prepared for the measurements. In addition, there were five compositions left from the work of Ufford⁴ in this laboratory in 1928. Ufford studied the resistance to 12,000 kg/cm^2 , not high enough to encounter any of the new effects found here. *Density.* The experimental values are given in Table I and shown graphically in Figure 1. Densities are given both for the virgin specimen and after exposure to 40,000 kg/cm^2 . The latter densities were measured within half an hour after release of pressure at room temperature, so that any error due to reversion of the compound should be small. It will be seen that at both ends of the composition range small increases of density are produced by

pressure, whereas in the middle of the range the effect is a much larger decrease of density. The relation between composition and density of the virgin alloy can be represented by two linear ranges joining at 39 At per cent with an error not anywhere greater than 0.02 on the density, except for the single point at 99 per cent Bi, where the deviation is 0.03. The densities at intermediate compositions are greater than would be given by a single straight line joining the two pure components.

TABLE I
DENSITY AT ATMOSPHERIC PRESSURE AT ROOM TEMPERATURE
Bi-Sn SERIES

Composition, At % Bi	Density		Change After Pressure
	Before Pressure	After Pressure	
100.00	9.788		
99.05	9.745	9.784	+0.039
97.98	9.759	9.763 (?)	+0.004 (?)
89.88	9.588	9.612	+0.024
79.89	9.391	9.350	-0.041
70.05	9.160	9.131	-0.029
63.27	9.014	8.879	-0.135
49.82	8.734	8.614	-0.120
43.4	8.578	8.568	-0.010
36.2	8.418	8.418	.000
29.72	8.212	8.222	+0.010
19.99	7.906	7.911	+0.005
10.08	7.608	7.626	+0.018
5.07	7.427	7.470	+0.043
2.05	7.340	7.365	+0.025
0	7.278		

The densities of this series have been previously determined by Thomas and Evans.⁵ Their values agree on the whole with mine within 0.02 or usually better, but with two perhaps important exceptions. At 12.4 and 25 At per cent their densities are 0.05 higher than my curve, and between 98 and 100 per cent Bi three compositions indicate a sharp maximum at 99 per cent at a density 0.08 greater than the density of pure Bi. I have only a single point in the close neighborhood of 99 per cent, but for this there is no rise but rather a drop of about 0.03 on the density below what would be indicated by a straight line. Preparation of other specimens would be desirable to straighten out the discrepancy.

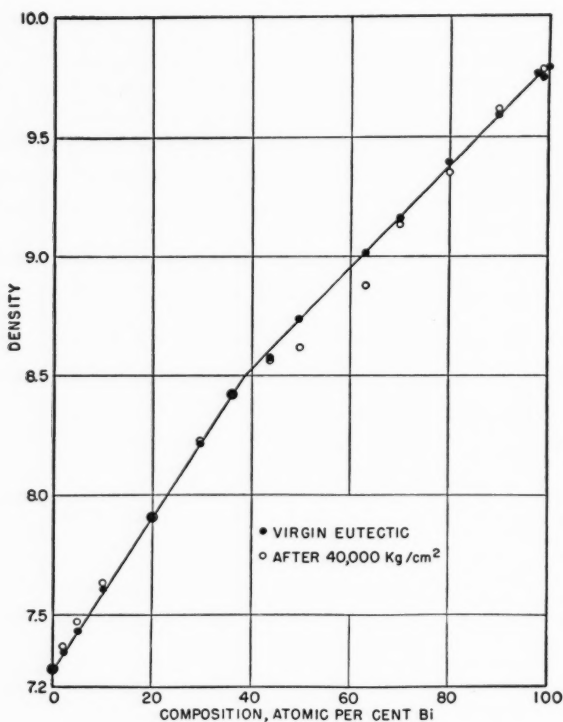


Figure 1. Densities of bismuth-tin alloys at atmospheric pressure at room temperature, before and after exposure to pressure, as a function of composition.

This I did not do because the principal interest of this work is in other ranges of composition.

Compressions to 40,000 kg/cm². Measurements were made with the same apparatus and with the same technique as my most recently published values on this same topic. All the alloys of the present series were soft enough mechanically so that the use of an indium sheath to equalize pressure was not necessary. Because of the permanent changes produced by the first application of pressure, two excursions to the maximum pressure were regularly

made on all specimens except the pure components, for which only single excursions were necessary. Although previous measurements had been made on the pure components, they were here repeated in the interest of greater uniformity.

Two sorts of information are given by the measurements. In the first place there are the volume discontinuities at the various transitions. Pure bismuth has two transitions in the general neighborhood of $25,000 \text{ kg/cm}^2$ with volume changes of roughly 4 per cent each. These transitions of the pure bismuth are also exhibited by the solid solutions of small tin content. The volume change associated with this transition diminishes as the total bismuth content becomes less through the series, but the pressures of the transitions experience no measurable change. These two transitions are so close together that they usually appeared as one with the present apparatus, being resolved only under especially favorable circumstances. In addition to the volume discontinuities to be ascribed to the bismuth transition, there is the volume change accompanying the formation of the intermetallic compound out of the virgin eutectic mixture. This is irreversible and usually does not occur until the pressure of the bismuth transition is nearly reached. It does not run sharply and often is running concurrently with the bismuth transition, which tends to obscure the results. Finally, there is the transition between the high and low pressure modifications of the compound. The transition from the high to the low pressure modification runs rapidly and apparently completely, but only with considerable overshooting of the pressure mark. One of the tasks of the measurements is to get the best parameters for these various transitions, allowing as well as possible for the fact that equilibrium is seldom if ever completely attained.

In addition to the volume discontinuities, there are the changes due to ordinary compressibility in the ranges where there are no discontinuities. It is a task of the measurements to get the volume compressibilities in the continuous ranges. This includes the initial virgin material and the various pressure modifications in their various mixtures with each other.

A. The volume discontinuities at the transitions. There is some uncertainty in disentangling the various transitions. Consider, for example, the case of volume creep toward smaller values on the first application of pressure at $23,000 \text{ kg/cm}^2$. Is this creep to be

ascribed to formation of the compound at a pressure beyond the equilibrium pressure between the two modifications of the compound, or is it to be ascribed to premature formation of the high pressure modification of bismuth, the normal equilibrium pressure having been lowered by the presence of tin in solution? It would perhaps have been impossible to obtain a satisfactorily consistent interpretation of all the transition phenomena if only the volume measurements were available, but fortunately the resistance measurements are also available, and the relations of the resistances are such as to remove possible ambiguities. When a transition runs because of increasing pressure the volume, of thermodynamic necessity, decreases, but the electrical resistance may either increase or decrease. Now the formation of the compound from the eutectic proves to be accompanied by an increase

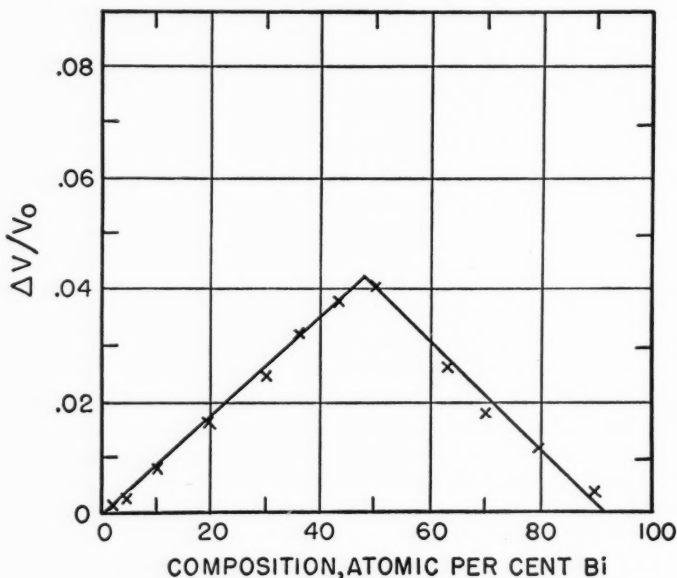


Figure 2. The discontinuity of volume when the high pressure modification of the compound, C II, forms from the virgin eutectic, as a function of composition.

of resistance, whereas the first high pressure transition of bismuth is accompanied by a large decrease of resistance. If then the creep of resistance at 23,000 is in the direction of an increase it means compound formation, whereas if it is a decrease it means the bismuth transition. It may be anticipated to say that it was always compound formation at this pressure; the normal transition pressure to the high pressure form of bismuth is not appreciably depressed by the tin in solution.

In Figures 2, 3, and 4 the several volume discontinuities are shown as a function of composition. Three discontinuities are to be considered: (1) the discontinuity when the high pressure modification of the compound (hereafter to be designated as C II) is formed from the virgin eutectic, shown in Figure 2; (2) the volume discontinuity accompanying the bismuth transition, which

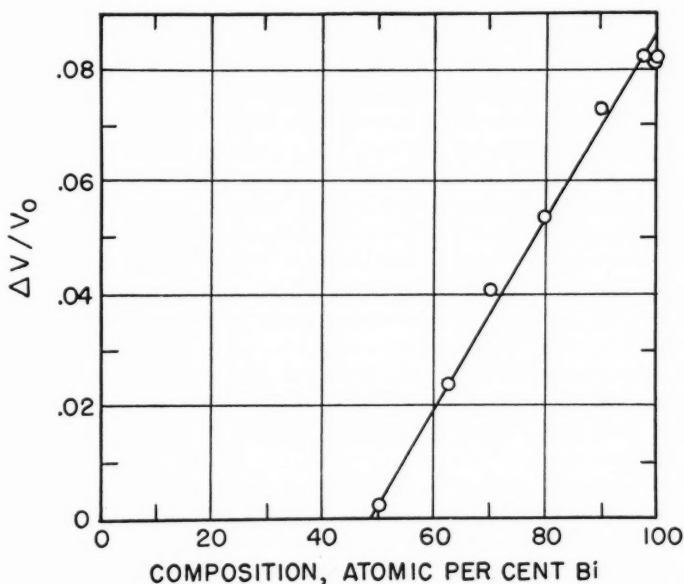


Figure 3. The discontinuity of volume accompanying the transition to the high pressure form of bismuth, Bi III, through the intermediate Bi II, as a function of composition.

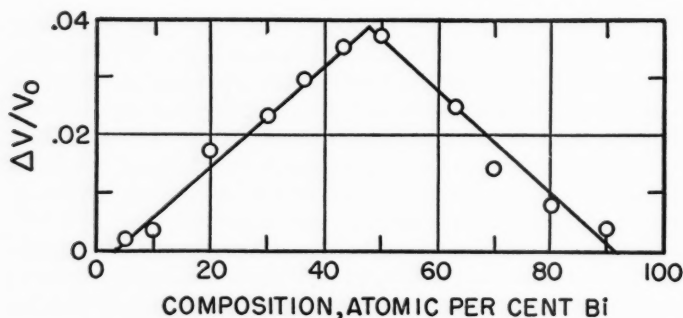


Figure 4. The volume discontinuity in the bismuth-tin system when the low pressure form of the compound, C I, changes to the high pressure form, C II, as a function of composition.

is actually two transitions, I-II and II-III together, being too close for resolution, shown in Figure 3; and (3) the discontinuity when the low pressure modification of the compound changes to the high pressure form, or vice versa, that is, for the transition C I to C II, shown in Figure 4.

Three independent measurements of (2) are possible: on first release, second increase, and second decrease of pressure. The average of the three is shown in the figure. The curves were so drawn through the observed points as to locate this transition at 25,000 kg/cm², very approximately the mean pressure from previous determinations. The mean pressure of the two transitions is actually 26,360 instead of 25,000 kg/cm². The difference between 25,000 and 26,360 involves an error in the volume discontinuity equal to the difference of compression of the two bismuth modifications over the pressure range of 1,360 kg/cm². This error is negligible.

Three independent measurements of (3), the volume difference between C I and C II, are also possible and on the same pressure excursions as for the bismuth transition. There is considerable sluggishness with respect to this transition, identical values for the volume not being obtainable with increasing and decreasing pressure without impractically long waiting, and not certainly even then. The discontinuities were usually located at 20,000

kg/cm² with increasing pressure and at 15,000 with decreasing. A negligible error due to difference of compressibility of the two forms is associated with this difference of 5,000. In general the transition with decreasing pressure ran more abruptly once it had started than the transition with increasing pressure.

The discontinuity (1) was given by only a single measurement for each set-up with each composition. This change runs so sluggishly that it was not possible to completely isolate it from the bismuth transition. Accordingly, the total discontinuity, bismuth transition plus volume change of formation of C II from the eutectic, was determined at 25,000 on the initial increase of pressure and the part due to formation of C II obtained by subtracting from the total the part due to the bismuth transition as already obtained under (2) as the mean of three measurements.

The discontinuities could not always be as cleanly analyzed as would be suggested by the description just given, but occasionally small satellite discontinuities appeared in addition to those just described. These are probably due to unusually large and capricious overshooting of the nucleation of the transition in isolated regions. In addition to this type of thing, there were a few instances where a small amount of the bismuth transition appeared at compositions where ideally it should not be present, namely at compositions with less than 50 At per cent bismuth on the second application of pressure. This is probably to be explained by a small reversion of C I to the eutectic during the lower part of the previous pressure excursion. It is known that C I reverts on standing at atmospheric pressure at room temperature, and there is no apparent reason why reversion should not take place more slowly at pressures higher than atmospheric.

Turning now to a consideration of Figures 2, 3, and 4, all three figures show a marked episode at approximately 50 At per cent bismuth. The bismuth transition does not run at all until the composition has reached 50 per cent bismuth; from this composition on the volume discontinuity increases linearly with the bismuth content. The interpretation is obvious. At less than 50 per cent bismuth all the bismuth is used up in pairing with atoms of tin to form the compound BiSn. Above 50 per cent bismuth there is an excess of bismuth after all the tin atoms have been paired with bismuth, and it is the excess bismuth which undergoes the

transition. The same interpretation applies with respect to the compound. The amount of compound present is a maximum at 50 At per cent, and on each side of this composition the amount of compound diminishes linearly with the amount of that component which is present in smaller amount. The linear relation between various volume discontinuities and composition indicates that in the aggregate there is little if any reaction between the microscopic grains, which probably take the form of a mechanical mixture without mutual solubility. This is consistent with the fact that the pressure of the two types of transition is constant, independent of composition. The principal argument for a compound of 50-50 composition is that the breaks in the volume discontinuities occur at this composition.

It will be noticed that the volume discontinuity shown in Figure 2 for compound formation is slightly greater than that in Figure 4 for compound transition. This means that at the pressure of equilibrium between C I and C II the compound is formed from the eutectic with slight loss of volume. Whether the volume relations are the same at atmospheric pressure depends on the relative compressibility of eutectic and C I over the 15,000 kg/cm² range back to atmospheric. It is obvious that if the density difference between eutectic and C I at atmospheric pressure really varies in the manner shown in the figure there must be slight departures from linearity between compressibility and composition.

B. The volume compressions in the continuous pressure ranges. The experiments disclosed four different sorts of continuous pressure range. There is in the first place the virgin material composed of a eutectic mixture of saturated dilute solution of tin in excess bismuth and a dilute saturated solution of bismuth in excess tin. This compresses uniformly up to the pressure of irreversible appearance of the high pressure modification of the compound C II. It must be recognized that in addition to the pure volume compressions under pressure there may be changes in the saturation limits with pressure. These changes would appear from these experiments to be small and they will be neglected. This first continuous pressure range on the virgin material terminates at between 20,000 and 25,000 kg/cm². The second continuous range also terminates at its lower edge at atmospheric pressure and embraces the low pressure modification of the compound, C I, and

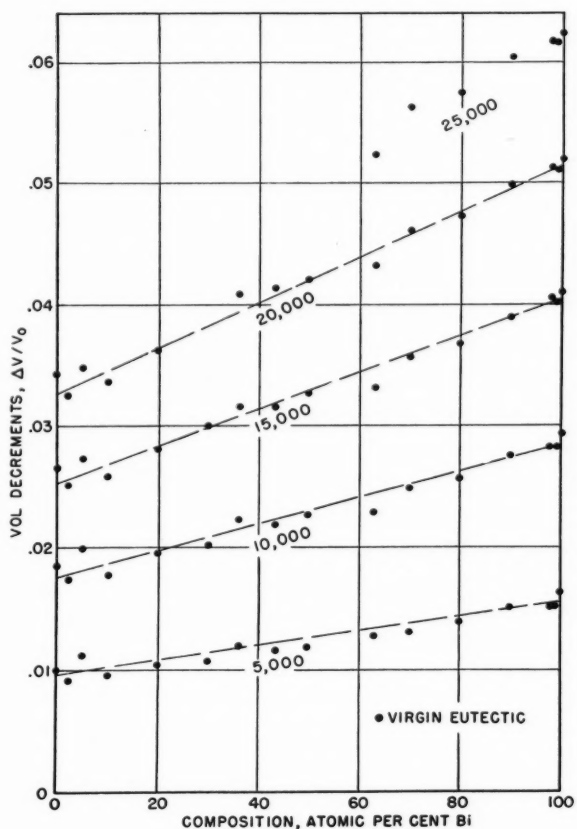


Figure 5. The volume compressions to the indicated pressures as a function of composition of the virgin eutectic in the bismuth-tin system.

either approximately pure tin or pure bismuth, depending on which side of 50-50 the gross composition lies. The upper limit of this range is 15,000 on release of pressure and 20,000 on increase. The third continuous range applies to the high pressure modification of the compound, C II, and either approximately pure tin or pure bismuth. Readings in this range can be obtained only with decreasing pressure between 25,000 and 15,000. Finally, the fourth

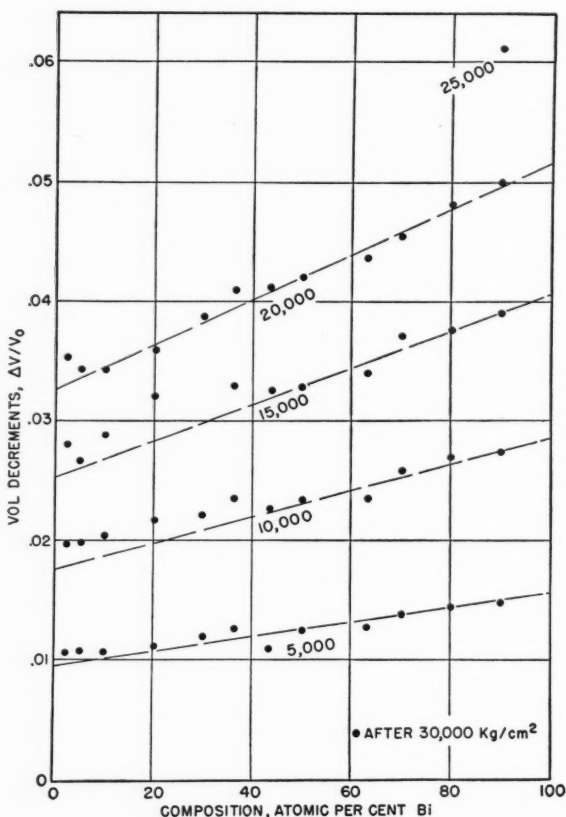


Figure 6. The volume compressions to the indicated pressures as a function of composition after exposure to pressure and irreversible formation of the low pressure modification of the compound, C I.

continuous range applies to C II and either approximately pure tin or bismuth. The range occurs above 25,000. For those compositions in which one of the constituents is approximately pure bismuth the bismuth exists in the form Bi III. Four sets of measurements can be made on this range: increasing or decreasing pressure on the two excursions to the maximum pressure.

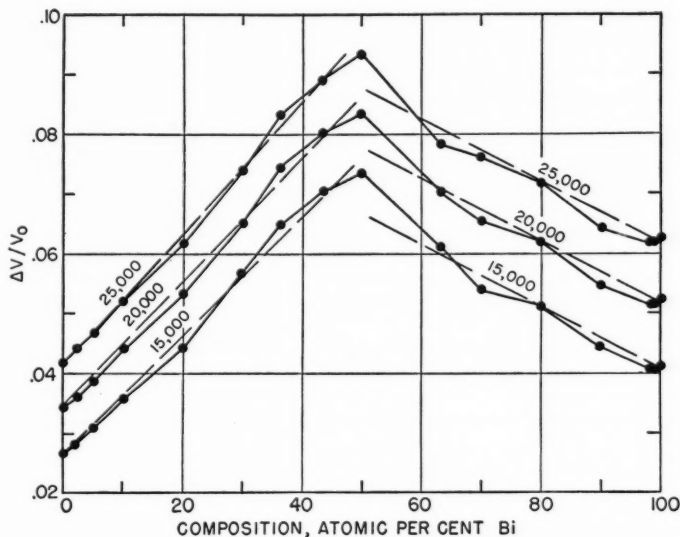


Figure 7. The volume compressions to the indicated pressures as a function of composition of the bismuth-tin system in that pressure range in which one of the components is the high pressure form of the compound, C II, and below the pressure of the appearance of the high pressure phases of bismuth.

Figures 5, 6, 7, and 8 show the volume compressions from atmospheric pressure for the four continuous ranges at 5,000 kg/cm² intervals of pressure as a function of composition. The "volume compressions" shown are $\Delta V/V_0$, where V_0 is the volume at atmospheric pressure of virgin material of the particular composition. If one wants to find the volume changes for systems of different compositions made up of the same total number of atoms, correction factors will have to be applied involving the initial density and the atomic weights.

The most striking feature of the four figures is that to a rough first approximation they are either linear in composition or are composed of two straight lines (Figure 7). This means that the volume decrements for any of the four ranges can be calculated from the corresponding volume decrements of the extreme compositions by simple linear interpolation. The volume decrements

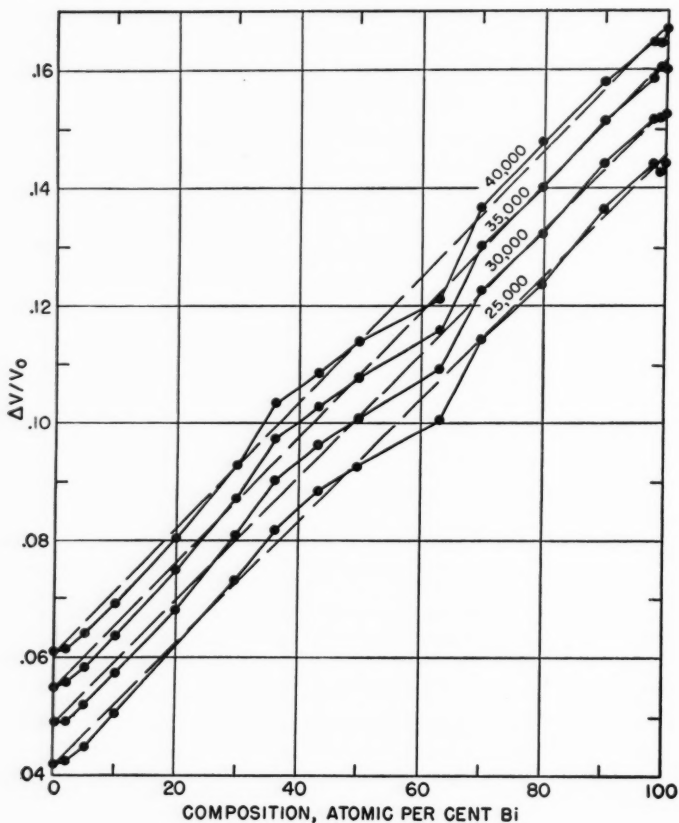


Figure 8. The volume compressions to the indicated pressures as a function of composition of the bismuth-tin system in the upper pressure range above the various transitions.

necessary in such a computation are given in Table II. It is to be emphasized that this table is to be used only for the purpose for which it was constructed, that is, to give fairly good approximations for the compressions over the entire composition range. It is highly probable that some at least of the deviations from linearity shown in the figures is real, but to establish this with any security

would demand extensive further experimenting. In particular, the table does not purport to give the best values for the compressions of the pure metals at the extremes of composition. For these, better values are at hand. It is merely that this table gives a summary for the intermediate compositions which is not far from the

TABLE II*
VOLUME DECREMENTS, $\Delta V/V_0$

Pressure kg/cm ²	Pure Bi	Pure Sn	Compound II
5,000	.0155	.0095	
10,000	.0285	.0175	
15,000	.0405	.0253	{ .0667
			{ .0760
20,000	.0514	.0326	{ .0778
			{ .0862
25,000	{ .0620	.0415	{ .0875
	{ .1455		{ .0960
30,000	.1535	.0490	
35,000	.1615	.0550	
40,000	.1676	.0605	

*See text for method of using this table.

present experimental error. The deviation from linearity is obviously greatest for the volume decrements of C II. For compositions not 50 per cent, a better approximation is obtained by using two straight lines on the two sides of 50 per cent with two different values for the volume decrement of C II. Of the two values given in the table for each pressure, the upper is to be used on the bismuth rich side of 50 per cent.

It was to be expected that the volume decrements above 25,000 should be given by *two* lines, meeting at a cusp, as for the system including C II between 15,000 and 25,000. For obviously the decrements for pure tin in this pressure interval do not include any phase transitions, whereas on the pure bismuth end the volume decrements include those of the phase transitions as well as the compressions above and below the transition. At 50 per cent composition the system is pure C II, and the corresponding volume decrement should be the volume discontinuity at the transition of C I to C II and the pure volume compressions of C I and C II below

and above the transition pressure. The fact that a single straight line instead of two reproduces the results means that the volume decrement just described associated with C II is the mean of the two decrements of pure tin and pure bismuth. This is a surprising relation. It means that in the compound each atom of bismuth or tin occupies approximately the same volume that it would occupy if that atom were seated in its own massive metal under the actually prevailing external pressure and *in the appropriate state of modification*. This simple statement is of course to be qualified by the second degree terms that appear on working out the analytic reduction from fractional changes of volume to actual number of atoms present, but the second degree terms are small and do not importantly modify the simple picture.

In line with the simple state of affairs disclosed in the last paragraph is the fact that the compressions of Figures 5 and 6, that is, the compressions for the system with virgin eutectic and for the system including C I, are approximately the same. This means that not only does C I form from the components with little change of volume, but that the compressibilities are also additive, something which evidently implies a higher degree of lack of interaction between the atoms than does the mere volume change on formation of the compound.

It is evident from the figures that the simple linear relations just discussed should be taken only as first approximations. It does not appear to what extent an attempt to obtain more refined information would be justified. There do seem to be certain consistent irregularities at the ends of the series in the neighborhood of the pure components. These may be correlated with the solid solutions which are supposed to exist at the two ends. The solubility limit of tin in bismuth is supposed to be only one or two per cent, whereas that of bismuth in tin has been given as much as 10 per cent. A difference in this direction in the solubility limits is suggested by Figure 5. Except for the one point at 5 At per cent bismuth, it would seem that the compressibility of either dilute solution is depressed compared with that of the pure metal. Most of the compressions associated with 63 At per cent bismuth in the figures are out of line by more than appears probably due to experimental error, and usually in the direction of too small a compression. No consistent correlation appears between deviation

from linearity in the figures and the permanent changes of density measured at atmospheric pressure after exposure to pressure. Clearing up these points would demand much more elaborate measurement.

Electrical Resistance. Measurements were made of the specific resistance at atmospheric pressure, of the temperature coefficient at atmospheric pressure, of the effect of pressures to 30,000 kg/cm² at room temperature, of pressure to 100,000 at room temperature, and various fragmentary studies of the secular changes taking place in the resistance after exposure to pressure in virtue of the irreversible transformations induced by pressure.

The material was extruded to wire of 0.020 inch diameter for the measurements, which were made by the potentiometer method with four leads. It might perhaps be feared that extrusion would introduce mechanical imperfections, such as incipient cracks. If so, there should be internal evidence of it in an abnormally rapid change of resistance for the first small increments of hydrostatic pressure. No such effects were ever found. Two sets of specimens were prepared, one for the measurements under pressure and the other for the various measurements at atmospheric pressure. For the pressure measurements the terminals were attached by soldering with ordinary lead-tin solder. For the measurements at atmospheric pressure the specimens were mounted in a jig with four spring contacts at fixed distances apart. By using a jig, all the atmospheric specimens were measured under standard conditions, which could be repeated after the lapse of time and exposure to temperature variations which might have loosened any soldered contacts. Certain irregularities in the potentiometer readings due to variable and high resistance at the spring contacts were eliminated by passing the current from a small magneto through the contacts before the readings.

A. Specific resistance at atmospheric pressure. Specific resistances at atmospheric pressure were measured for 20 different compositions. These measurements were made at room temperature, at 0°C, and then back at room temperature again. The check reading at room temperature was made in order to be sure that no internal change had been induced by the temperature change. None such was found. From these readings were calculated both the specific resistance at 0°C and the mean temperature coefficient

between 0° and room temperature in terms of the resistance at 0° . In calculating the specific resistance the mean diameter of the wire was used as determined by six micrometer readings to 0.0001 inch. The wires were fairly uniform and any error in specific resistance from uncertainty in dimensions should be a fraction of one per cent. After these measurements, all twenty wires were exposed simultaneously to $30,000 \text{ kg/cm}^2$, a pressure high enough to induce complete transformation to the compound. The wires so exposed were then remeasured for specific resistance and mean temperature coefficient between 0° and room temperature. In order to minimize any internal changes during the measuring process all wires were kept at dry ice temperature except during the actual operation of measurement, which might consume some twenty minutes. The specimens were then stored in dry ice, and remeasured after the lapse of two weeks for secular changes. They were then kept

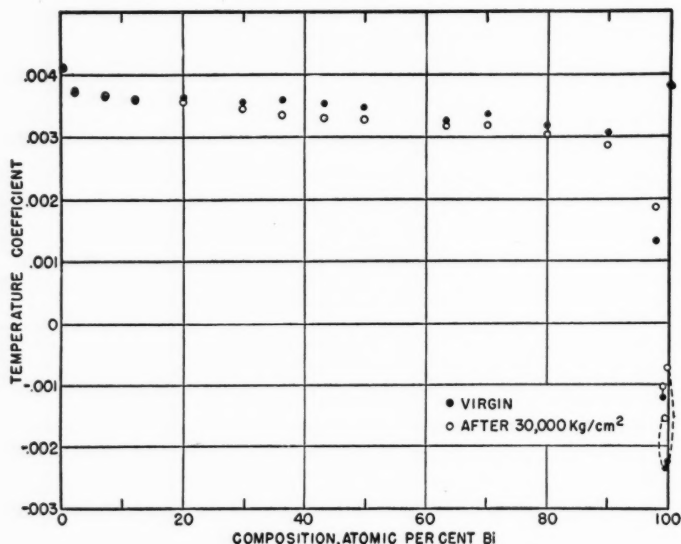


Figure 9. The specific resistance at atmospheric pressure at 0°C of the bismuth-tin system as a function of composition, except for dilute solutions of tin in bismuth, before and after exposure to pressure.

at 100°C for 12 hours and remeasured at room temperature for further secular changes.

The specific resistances at 0° at atmospheric pressure are shown as a function of composition in Figures 9 and 10. The first addition of tin to pure bismuth is seen to result in a large increase of resistance, amounting to nearly sixfold at approximately one per cent tin.

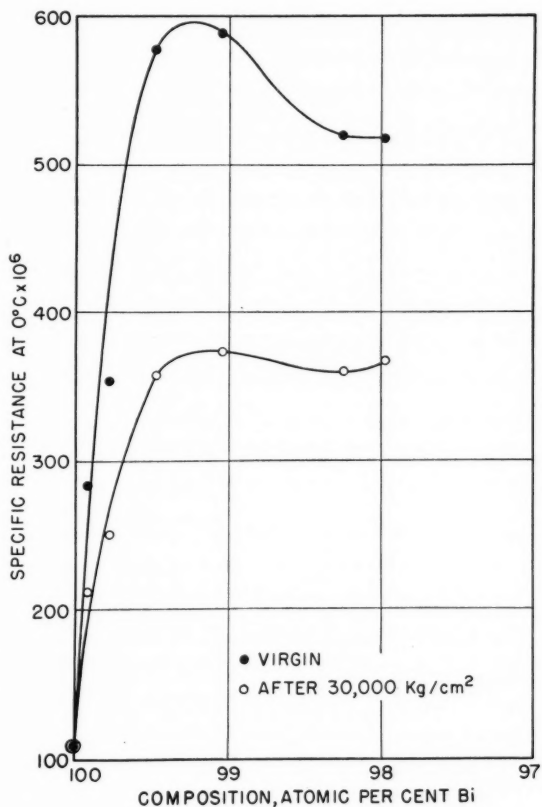


Figure 10. The specific resistance at atmospheric pressure at 0°C of the bismuth rich concentrations of the bismuth-tin system before and after exposure to pressure.

The specific resistance of this series has also been measured by Thomas and Evans.⁵ The agreement on the tin side up to 50 At per cent tin could perhaps be called satisfactory, but between 50 and 100 per cent bismuth there are wide discrepancies, for which the explanation does not appear. What is worse, the sign of the discrepancy varies. At 90 per cent bismuth their specific resistance is 275×10^{-6} against my 142×10^{-6} , whereas their maximum occurs at 98 per cent with a specific resistance of 393×10^{-6} against my maximum at about 99 per cent with a specific resistance of 588×10^{-6} .

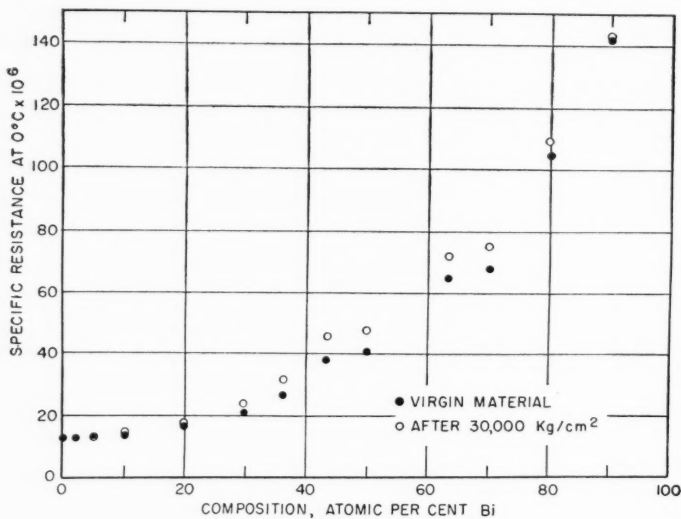


Figure 11. The mean temperature coefficient of resistance between 0°C and room temperature of the bismuth-tin system as a function of composition, before and after exposure to pressure.

Discussion of the various changes of resistance after exposure to pressure will be deferred until after presentation of the pressure effects.

B. Temperature coefficient of resistance at atmospheric pressure. The temperature coefficient of resistance between 0°C and room temperature is shown in Figure 11. It will be seen that the first

small additions of tin to bismuth result in a very rapid depression of the temperature coefficient, with change of sign to a minimum of -0.00237 at 0.2 At per cent Sn, followed by a rapid recovery to positive values, which remain between 0.003 and 0.004 over the entire range of composition from 10 per cent tin to pure tin. It is to be noticed that the minimum temperature coefficient occurs earlier than the maximum of specific resistance, namely at 0.2 per cent against approximately one per cent.

The temperature coefficient between 0° and 30° has also been given by Ufford.⁴ He too finds the reversal of sign at a small concentration of tin, but the numerical agreement is not good. The smallest coefficient which he found was -0.00044 at 0.53 At per cent tin. There seem to have been considerable experimental irregularities in his work, because the curve which he draws for the best temperature coefficient fails by a rather wide margin to pass through all the experimental points. Doubtless the explanation of the most important part of the discrepancy at low tin concentrations is insufficient purity in Ufford's bismuth. His alloys were made up with Kahlbaum "K" bismuth, and his compositions are given in terms of it. The temperature coefficient of this was only 0.0028 against 0.00383 for the purified bismuth used in making the present series of alloys.

C. Effect of pressure up to 30,000 kg/cm² on resistance. Measurements were made on 26 different specimens, including five 24-year-old specimens left from the work of Ufford. The latter had been kept sealed in glass under nujol. The pressure phenomena are highly complex, and, short of reproducing all the original data, can be described only with a certain amount of conventionalization. There are several regions of unusual effects. In the first place, the region of dilute solution of tin in bismuth is unusual in the nearly sixfold increase in resistance accompanying only one per cent of tin. The resistance in this region is to be thought of as the resistance of pure bismuth plus an "additive" resistance due to the foreign atoms of tin. This additive resistance appears to be abnormally sensitive to pressure, being in general decreased by it, so that the total pressure effects in this region exhibit reversals of curvature and points of inflection. One sort of phenomenon which might have been anticipated in this region did not manifest itself however; namely, changes in the solubility limits produced by

pressure accompanied by solution or unsolution effects with corresponding creep of the resistance. No creep effects were found on the first application of pressure to the virgin alloy until a transition pressure had been reached, and all creep effects, of which there were many, appeared to be associated with one or another of the transitions. These transitions were the same as those already met in the volume measurements. First is the irreversible formation of the high pressure modification of the compound on first increase of pressure. In general, resistance increases during this change except at low tin concentrations where the additive resistance is high. Here, resistance decreases on formation of C II because of disappearance of the high additive resistance. The irreversible formation of C II takes place, except at low tin content, throughout the region 20,000 to 25,000 kg/cm² and is sluggish and pressure sensitive. That is, one may wait at, say, 23,000 kg/cm² a sufficient time for the reaction to apparently complete itself, and then on increasing pressure to 24,000 the reaction runs some more. At low tin content, below 30 per cent, C II forms only simultaneously with Bi II, that is, above 25,000 kg/cm².

Next, on increase of pressure, there is the transition to Bi II. This runs with large decrease of resistance, sixfold or more for pure bismuth, and is always a comparatively clean-cut and rapid reaction, being completed within a pressure interval of the order of 1,000 kg/cm².

Next, on increase of pressure, occurs the transition from Bi II to Bi III, accompanied by an increase of resistance, which for pure bismuth is two or threefold. Because of the reversal of direction of the changes of resistance it was easy to resolve the two transitions of bismuth by means of the resistance measurements, although they were usually fused together for the volume measurements. On release of pressure the two bismuth transitions may with care be found in the inverse order. The transition III to II, however, has a strong tendency to overshoot on release of pressure and may not occur until the transition pressure between II and I is passed. The appearance then is as if there were direct passage from III to I. Whether there is actually intermediate formation of II would be difficult to establish, but the probability is in favor of it because creep has been observed in both directions in this region. The region of several thousand kg/cm² below 25,000 on release of

pressure is likely to be a region of creep, and this region may extend so far that the creep begins to be mixed up with the transition from C II to C I. This transition also runs throughout a region with no clean-cut limits. The speed of the transition tends to become greater at lower pressures and increases so rapidly that there is a sweep in the neighborhood of 15,000. Below 15,000 the transition is completed, creep disappears, and the system under measurement consists of so much of C I as is yielded by the gross composition plus approximately pure tin or pure bismuth as the case may be.

Added to all the complications due to phase changes there are smaller complications arising from the non-cubic nature of the pure components and presumably of the alloys, with corresponding non-isotropy of resistance. This means that on passing back and forth through a transition the original resistance will not be recovered unless the original orientation is recovered. It is known that transitions may be divided into two classes according as the original orientation is recovered or not. Orientation is not recovered in the bismuth I-II transition, so that resistance measurements on pure bismuth in the region below 25,000 are in general not completely reversible after an excursion above 25,000, although the failure is usually small. The irreversibility is plainly apparent in the appearance of the wire after a pressure excursion, which is full of small roughnesses and offsets. After a cycle with transition there was in general a permanent change of length, usually a decrease, by an amount seldom if ever greater than one per cent. In computing the permanent change of specific resistance after a pressure run allowance was made for the permanent change of length, assuming no permanent change of density.

The II-III transition of bismuth, unlike the I-II transition, appears to be reversible with respect to orientation. It would appear that the C I-C II transition is not reversible with respect to orientation, because on passing back and forth through the transition the resistances do not repeat. However, these effects are small, only a few per cent on total resistance.

In general the creep effects in the resistance measurements were much more capricious than in the volume measurements. This is probably associated with the difference in geometrical shape of the specimens, a massive hunk in the one case and a long slender

TABLE III
SPECIFIC RESISTANCE $\times 10^6$ OF BISMUTH-TIN SERIES

Pressure Kg/Cm ²	0		5,000		10,000		15,000	
100% Bi	109.00		119.78		131.94		145.63	
	Increase	Decrease	Increase	Decrease	Increase	Decrease	Increase	Decrease
99.916% Bi	235	213.1	271.1	232.6	307.8	249.0	339.2	262.7
99.779% Bi	367.0	292.6	408.2	303.7	438.5	309.0	456.1	311.6
99.485% Bi	509.	331.9	524.0	326.6	522.0	318.4	508.8	308.4
99.051% Bi	588	373.2	576.0	358.1	552.4	343.9	524.0	326.0
99.051% Bi†	599.6	433.0	581.4	413.2	555.5	393.8	523.8	371.1
98.25% Bi	582.0	397.0	551.6	377.5	514.6	355.6	476.8	331.3
97.98% Bi	551.6	400.5	533.5	383.3	507.4	365.4	478.8	346.7
95% Bi*	266.5	240.9	257.6	230.8	248.7	219.8	238.4	343.7
90% Bi*	151.6	141.0	145.5	135.1	139.3	129.2	133.3	210.2
89.88% Bi	203.6	195.6	192.7	186.7	181.9	176.9	172.2	193.2
80% Bi*	104.5	105.5	99.8	100.7	95.5	96.2	91.5	123.2
79.89% Bi	122.6	155.4	116.4	148.0	110.3	139.7	104.7	167.5
70.05% Bi	68.2	88.00	64.6	83.68	61.28	79.52	58.34	92.1
63.27% Bi	71.9	85.32	68.1	81.6	64.7	77.9	61.6	132.5
49.8% Bi	44.75	58.20	42.50	55.72	40.50	53.25	38.70	113.0
43.4% Bi	33.84	45.32	32.30	43.12	30.97	41.16	29.68	76.20
43.4% Bi†	33.84	44.20	32.27	42.30	31.02	40.51	29.73	63.2
36.2% Bi	23.87	26.80	22.88	25.72	21.99	24.71	21.16	74.4 C I
29.72% Bi	24.47	28.40	23.40	27.14	22.48	26.04	21.68	63.3 C II
19.99% Bi	16.28	17.95	15.60	17.20	15.00	16.53	14.46	51.00
10.08% Bi	15.08	15.68	14.49	15.03	13.93	14.46	13.41	39.47
5.07% Bi	13.93	14.10	13.36	13.50	12.85	12.97	12.43	32.34
	Increase-Decrease		Increase-Decrease		Increase-Decrease		Increase-Decrease	
2.05% Bi	14.11		13.55		13.00		12.52	
100% Sn	13.520		12.852		12.277		11.774	

† 2nd specimen.

* Ufford's specimen.

TABLE III
SPECIFIC RESISTANCE $\times 10^6$ OF BISMUTH-TIN SERIES

20,000		25,000		30,000	Pressure Kg/Cm ²
160.66		178.66		<div> <div>23.9 II at 26,000</div> <div>98.2 III at 27,000</div> </div>	100% Bi
Increase	Decrease	Increase	Decrease	Increase	
367.8	276.7	392.8	286.1	75.0 III at 27,000	99.916% Bi
		28.4 II		73.4 III at 30,000	
467.9	314.1	474.0	316.3	75.2 III at 27,000	99.779% Bi
		28.3 II		73.6 III at 30,000	
487.2	297.0	460.0	286.0	75.6 III at 27,000	99.485% Bi
		28.4 II		74.5 III at 30,000	
491.4	308.0	455.5	288.9	75.8 III	99.051% Bi
		28.6 II			
491.2	349.0	457.3	323.7	78.0 III	99.051% Bi†
		30.2 II			
437.7	302.6	27.9 II		73.0 III at 27,000	98.25% Bi
				72.6 III at 30,000	
447.8	327.2	415.8	310.5	74.7 III at 27,000	97.98% Bi
		29.5 II		74.0 III at 30,000	
229.7	183.6	219.8	175.2	65.0 III at 27,000	95% Bi*
		27.0 II		64.3 III at 30,000	
127.6	116.7	23.2 II	106.8	49.2 III at 27,000	90% Bi*
	112.7 ²			48.2 III at 30,000	
163.5		30.7 II			89.88% Bi
88.2		85.3		46.6 III at 27,000	80% Bi*
		27.2 II		45.8 III at 30,000	
99.9	106.8				79.89% Bi
106.8					
55.40	73.02	57.15		42.50 III at 27,000	70.05% Bi
59.86	60.0	31.80 II		41.77 III at 30,000	
58.8		58.48 C II			63.27% Bi
60.90 C II		30.61 II			
				34.04	49.8% Bi
28.40		29.64		27.89	43.4% Bi
30.72		28.30			
28.08		30.00		29.14	43.4% Bi†
31.07					
20.50		20.52		19.93	36.2% Bi
21.23					
20.97		20.48		19.80	29.72% Bi
21.40					
14.03		14.00		13.52	19.99% Bi
14.54					
12.95		12.68		12.26	10.08% Bi
13.14					
11.99	12.04	11.65		11.23	5.07% Bi
Increase-Decrease		Increase-Decrease		Increase-Decrease	
12.09		11.70		11.34	2.05% Bi
11.302		10.887		10.509	100% Sn

† 2nd specimen.

* Ufford's specimen.

wire in the other. With the wire it would appear to be easier for the transition in one part of the wire to get isolated from the rest, so that completion of the transition throughout the whole wire might require several independent nucleations.

A complete summary of the experimental results on all specimens, smoothed and conventionalized at 5,000 kg/cm² intervals, is given in Table III. The many gaps in the table correspond to regions with too much creep to justify unique values. Selected results from the table are shown in Figures 12, 13, and 14. Figure 12 is for the middle of the very dilute tin range, where specific

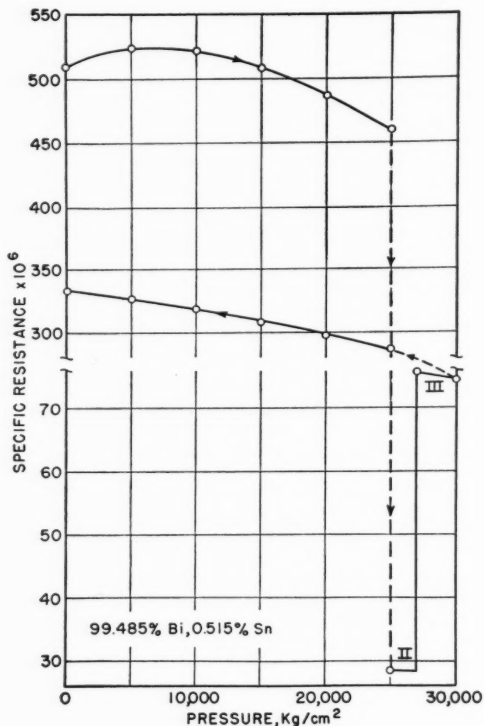


Figure 12. The specific resistance as a function of pressure for a dilute solution of tin in bismuth.

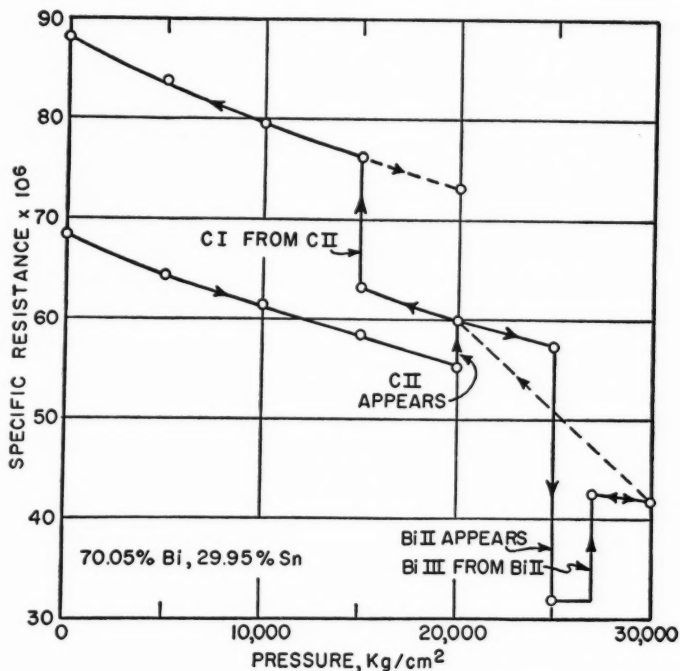


Figure 13. The specific resistance as a function of pressure for a bismuth-tin alloy for a composition showing all the transitions.

resistance is high and very sensitive to composition. Figure 13 is in the middle of the bismuth rich end where the two bismuth transitions dominate, and Figure 14 is in the middle of the tin rich end, where the bismuth transitions have dropped out and the formation and transition of the compound dominates.

In the following a verbal description will be given of the data presented in the table and figures. The descriptions will be grouped around the various homogeneous ranges.

First, consider the effects on the virgin material, before the entry of either bismuth II or C II, that is, the range up to 25,000 kg/cm² for smaller tin concentrations and to 20,000 for larger concentrations. We have already seen that the result of initial addition of

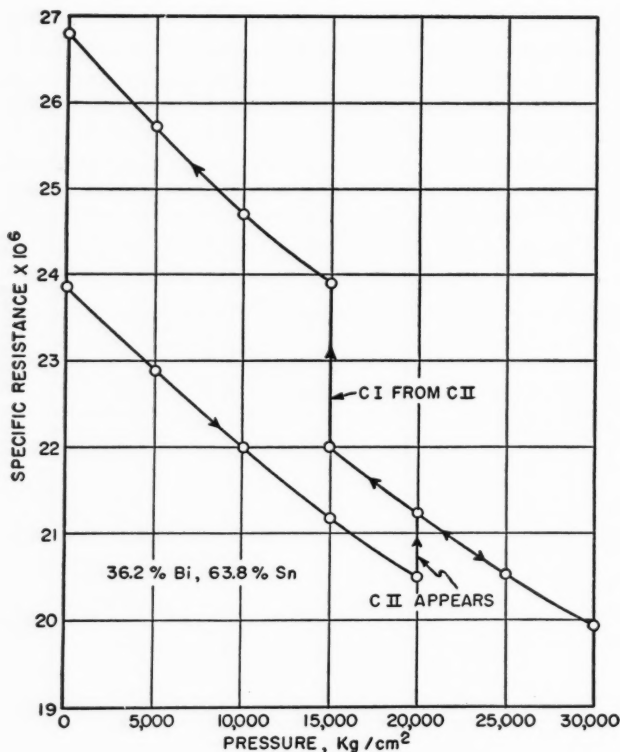


Figure 14. The specific resistance as a function of pressure for a bismuth-tin alloy for a composition in the tin rich range where the only transitions are those of the compound.

tin to bismuth up to one per cent tin is a very rapid rise of specific resistance to nearly 600×10^{-6} against 109×10^{-6} for pure bismuth. The resistance of pure bismuth against pressure rises at an accelerated rate, that is, with upward curvature. The effect of the initial small addition of tin of 0.084 per cent is to more than double the specific resistance and also to greatly increase the initial pressure coefficient of specific resistance, although not by as large a factor as the specific resistance. Increase of resistance with pressure

at this composition is at first concave upward, but the curvature presently reverses, and for the range above 10,000 and up to 25,000 the increase of resistance is concave downward. This is a highly unusual kind of resistance change and few examples are known. With increasing tin content, and still in the region of increasing initial specific resistance, the initial pressure coefficient becomes less and the transition from upward to downward curvature is displaced to lower pressures so that presently the curve is concave downward from the beginning. At 0.5 At per cent tin, shown in Figure 12, the downward concavity has become so large that there is a resistance maximum at less than 10,000 kg/cm². On further increasing the tin content to the composition of maximum specific resistance at atmospheric pressure, resistance drops with increasing pressure from the beginning and still with abnormal downward curvature. With further increasing tin content specific resistance drops, the pressure coefficient becomes less and the curvature less. Presently a point of inflection with reversal of curvature appears at the highest pressures; this point of inflection works toward lower pressures with further increasing tin content and reaches the middle of the pressure range at about 10 per cent tin. At higher tin content the curve becomes normally concave upward over the entire pressure range. There is no special episode on the tin rich end of the series, and therefore no evidence from these resistance measurements of any solubility of bismuth in tin.

Consider next the first bismuth transition, from I to II. This dominates the situation on the bismuth rich end of the series, but disappears beyond 50 At per cent tin, all the bismuth being used up in forming the compound. At low tin concentrations the first transition encountered is the Bi I-II transition. Ideally this should be preceded by the formation of C II. At small tin concentrations the formation of C II would be difficult to detect, the amount being proportional to the tin content. But as the tin content increases one would expect to encounter the formation of C II in no unmistakable terms. As a matter of fact the formation of C II prior to the bismuth I-II transition did not show up until 30 At per cent tin was reached. It would appear that C II forms much more readily from a matrix in which bismuth II is present than from one with bismuth I. When the Bi I-II transition does run it is to be presumed that formation of C II occurs simultaneously.

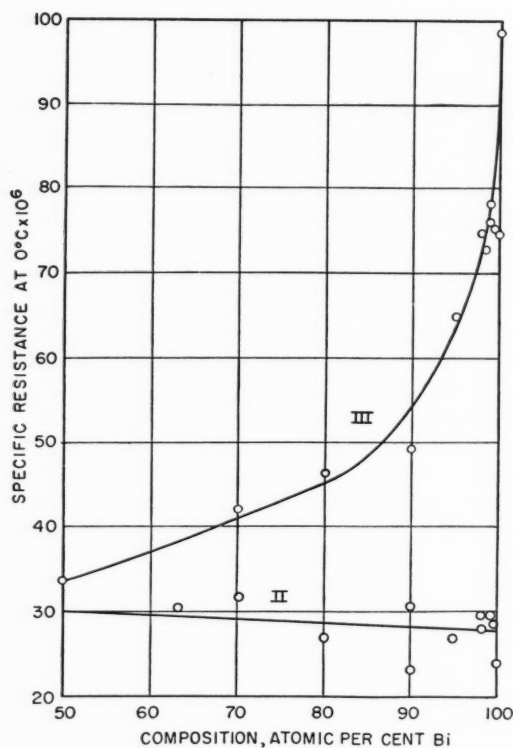


Figure 15. The average specific resistances above 25,000 kg/cm² for bismuth rich compositions in the bismuth-tin system in which one of the components is Bi II or Bi III.

In Figure 15 are shown the average specific resistances above 25,000 kg/cm² of the systems containing Bi II or Bi III. The system in the pressure region above 25,000 and below the Bi III transition at about 27,000 consists of Bi II and C II mixed in proportions corresponding to the gross composition. Now the figure shows that the specific resistance of this system is approximately constant over the entire composition range down to 50 per cent Bi. This constancy is attained in the face of a drop of resistance at

the transition from Bi I to Bi II by as much as a factor of 20 at low tin concentrations. Two probable conclusions would seem to be indicated by this. The first is that there are no solution phenomena of tin in bismuth II corresponding to the solution of tin in bismuth I which is responsible for the initial great increase of specific resistance. That is, one of the components of the system between 25,000 and 27,000 is probably *pure* bismuth II. The other conclusion is that the specific resistance of C II must be close to that of Bi II, for otherwise the resistance of the whole system would not remain constant during the change in the proportions of Bi II to C II from infinity to zero which occurs in the range of 50 per cent gross bismuth.

Above 27,000 kg/cm², where Bi III has formed, Figure 15 shows the specific resistance is not constant, but drops with increasing tin content from 98×10^{-6} to approximately the value of Bi II and C II. The explanation is consistent with that of the last paragraph. The specific resistance of Bi III is *not* the same as that of C II, but is several fold greater. Hence as the composition of the system varies from all Bi III to all C II the total resistance varies accordingly.

At tin contents higher than 30 At per cent the irreversible formation of C II usually occurs at a pressure markedly below the Bi II point, in the general neighborhood of 20,000 kg/cm². There is nothing sharp about the onset of this transition, either with respect to pressure or composition. On one occasion it was possible to make systematic measurements on it at a composition of only 10 per cent tin.

At 50 per cent tin the Bi II transition disappears and C II becomes the only transition with increasing pressure. The discontinuity of resistance accompanying the formation of C II becomes progressively smaller with diminishing bismuth content, since the amount of the phase C II formed becomes smaller. Evidence of the formation of C II was lost between 10 and 5 per cent bismuth. As already remarked, the formation of C II may be accompanied by an overall increase of resistance. It might appear at first as though there is here an inconsistency with the statement that the specific resistance of C II is approximately the same as that of Bi II. There is no inconsistency, however, when the absolute values of resistance are considered. The increase occurred only with

compositions where the tin content was so high that the total resistance of the system was less than that of pure Bi II.

On release of pressure from 30,000, the first transition encountered with the bismuth rich compositions was Bi III to Bi II. There was not so much interest in this transition and careful readings were not always made on it. Next was encountered the Bi II to Bi I transition. This was not the reverse of that with increasing pressure, because now the end product included as much of C II as was permitted by the gross composition. Below the Bi II point there was a range, extending down to the general neighborhood of 15,000, in which the system comprised C II plus the mixed Bi-Sn system. At 15,000, or over a range with 15,000 as the lower edge, the transition C II to C I occurred. This runs with increase of resistance. No very consistent values were obtained for the numerical magnitude of this increase because of the capriciousness of the transition between 20,000 and 15,000, hysteresis and delayed starting being by no means reproducible. A rough trend could be established, however. At the bismuth rich end of the series the increase of resistance of the whole system at the transition increases to a rough maximum in the neighborhood of 20×10^{-6} and 75 At per cent Bi, dropping to something of the order of 10×10^{-6} at 50 At per cent Bi. Here the system is presumably all in the state C I, so that the actual specific resistances are the specific resistances of pure C II and C I. These values were 40×10^{-6} for C I and 50×10^{-6} for C II, which are the presumptive values at 15,000 kg/cm².

The delay and creep phenomena in the region 15,000 to 20,000 are complex and often capricious; explanation along the comparatively simple lines suggested above could not always be defended against deliberate attack. However, no alternative explanation along more complicated lines seemed indicated with sufficient definiteness to take seriously. If ever this system is re-examined with greater elaborateness, the question which I believe should be examined most carefully is whether there are not three modifications of the compound in this region, with transition pressures so close that they cannot be easily resolved, analogous to the close transitions of pure bismuth.

Finally, below 15,000 on release of pressure, the system consists of so much of C I as permitted by the gross composition, plus

approximately pure bismuth or tin. Except at very low tin concentrations, up to about 0.2 At per cent Sn, the pressure coefficient has the normal negative sign. In the very dilute region, there are reversals of direction and curvature analogous to those on initial increase of pressure, which can be evaluated in detail from the data in Table III. In the region of low tin concentrations, where the specific resistance is high, the specific resistance of the final system is less than that of the initial system. Between 10 and 20 per cent this reverses sign, and over most of the range the final system with C I has a higher specific resistance than the virgin system. As a function of pressure, the two curves, on initial application and final release, run nearly parallel, so that the pressure coefficient of the two systems is nearly the same.

The question arises as to what the other component is besides C I in the system after release of pressure. On the bismuth rich end it might conceivably be pure bismuth, but this seems unlikely, because in the region of high tin dilution even the final resistances are too high to be accounted for by any combination of pure bismuth and C I. It would seem probable that at high dilution most of the tin is removed from the original solution to form the compound, but that enough is left in solution at the saturation composition to bring the total resistance to the observed value. If the final system is assumed to consist of three components, saturated solution of tin in bismuth, compound, and saturated solution of bismuth in tin, then the distribution among the three components demanded by the phase rule is indeterminate. If, however, it is assumed that on the bismuth rich end there is no saturated solution of bismuth in tin, and on the tin end no saturated solution of tin in bismuth, then the distribution becomes determinate. Whether this is a plausible state of affairs or not could then be told by comparing the calculated resistance of such a system with the observed resistance. This calculation cannot be made without an assumption about the nature of the geometrical entanglement of the grains of the different components with each other. The question of the constancy of the method of entanglement would then arise. So far I have not attempted such a calculation.

The final system on releasing pressure containing C I is not stable with respect to the original system, at least at atmospheric pressure. The inverse reaction runs at room temperature with

observable velocity at atmospheric pressure, but in the natural time of observation of the experiments, of the order of ten minutes, no inversion was observed at pressures higher than 2,500 kg/cm². At atmospheric pressure the rate is so low at room temperature that the observations as obtained without special precautions should give with good approximation the resistance at atmospheric pressure of the system formed from C II at 15,000.

D. *Behavior of resistance at atmospheric pressure after exposure to pressure.* We return now to the topic left in abeyance on page 122. In Figure 16 are shown the ratios of the specific resistances at atmospheric pressure and room temperature before and after completion of a pressure cycle to 30,000 kg/cm² with irreversible formation of C I. The information in Figure 16 is contained in

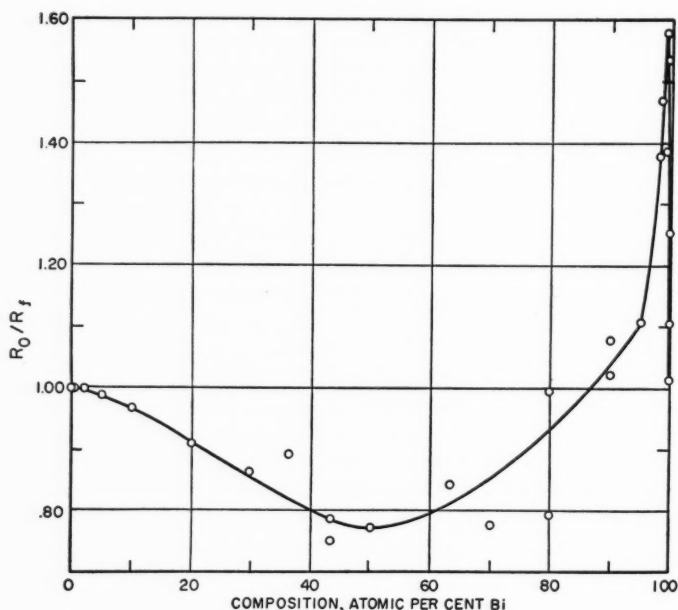


Figure 16. The permanent change in resistance, as a function of composition, in the bismuth-tin system after exposure to pressure. Essentially the same information, on another scale, is contained in Figures 9 and 10.

another form in Figures 9 and 10. There is considerable irregularity, but the general trend is unmistakable. At low tin concentrations there is a large decrease of resistance after the pressure cycle, rising to a maximum at 1 At per cent Sn where the specific resistance of the virgin material is also a maximum, dropping after the maximum to zero at about 10 per cent tin, followed by a more gentle increase which has its maximum at 50 At per cent.

Both the pressure and the temperature coefficients of the final system with C I are different from those of the virgin system. The temperature coefficients before and after subjecting to the pressure cycle have already been shown in Figure 11. The corresponding values for the pressure coefficients at atmospheric pressure are shown in Figure 17. The atmospheric pressure coefficients are also shown in Table IV. These coefficients were

TABLE IV
INITIAL PRESSURE COEFFICIENTS

Composition	Before 30,000	After 30,000
100 Bi	$+1.87 \times 10^{-5}$	
99.916	+2.97	$+2.01 \times 10^{-5}$
99.779	+2.52	+1.05
99.485	+0.974	-0.228
99.051	-0.136	-0.895
	-0.473	-0.965
98.25	-0.858	-0.923
97.98	-0.436	-0.843
95.U	-0.705	-0.823
90.U	-0.805	-0.835
89.88	-1.09	-0.880
80.U	-0.938	-0.930
79.89	-1.03	-0.912
70.05	-1.094	-0.977
63.27	-1.096	-0.900
49.8	-1.057	-0.859
43.4	-0.975	-1.025
	-1.034	-0.907
36.2	-0.87	-0.822
29.72	-0.930	-0.950
19.99	-0.870	-0.88
10.08	-0.805	-0.872
5.07	-0.877	-0.821
2.05	-0.810	
100 Sn	-1.05	

found by calculating $\frac{\Delta R}{R_0} \cdot \frac{1}{p}$ at 5,000, 10,000 and 15,000 kg/cm² and extrapolating to zero pressure. In the region of small tin concentrations there may be large changes in these coefficients, but over most of the composition range the changes are comparatively small, and usually in the direction of a numerical decrease of coefficient after the pressure cycle. Table IV shows that the first addition of a small amount of a second component at either end of the composition range has the effect of numerically increasing the pressure coefficient of resistance. As far as I know this rule is without exception.

A few observations were made of the secular changes after a pressure cycle. There are in the first place the observations already

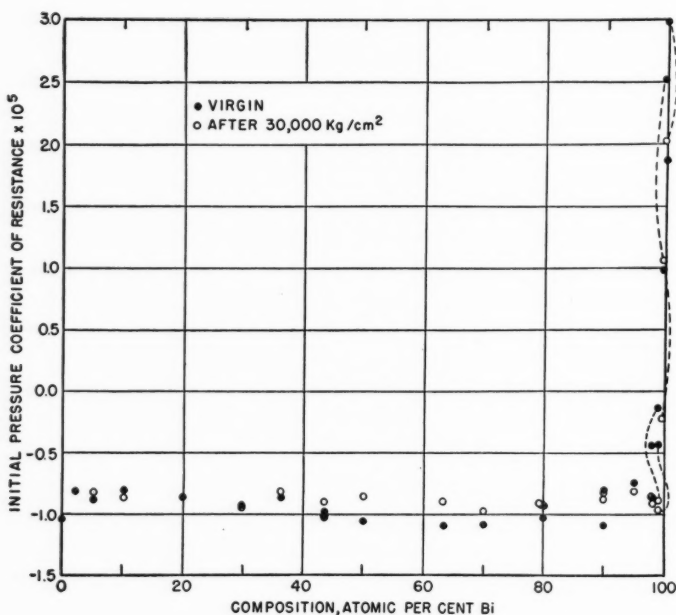


Figure 17. The initial pressure coefficient of resistance (that is, the coefficient at atmospheric pressure) of the bismuth-tin system as a function of composition, before and after exposure to pressure.

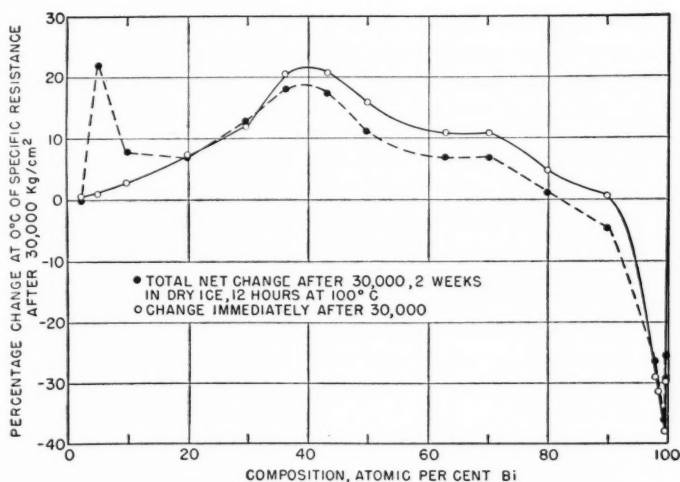


Figure 18. Secular changes of specific resistance in the bismuth-tin system after exposure to pressure.

referred to of the changes of resistance at 0°C after holding at dry ice temperature for two weeks and then at 100° for 12 hours. These results are shown in Figure 18. It will be seen that over most of the composition range exposure to 100° is followed by partial return to the resistance of the virgin specimen, but there are several notable exceptions, particularly at the tin rich end of the series.

The most extensive observations of secular change after 30,000 were made on the composition 70.05 Bi – 29.95 Sn. The resistance of this after the first exposure to pressure increased by 29 per cent, an unusually large amount, and quite out of line with the values shown in Figure 18. A second exposure to the 30,000 cycle was then made with negligible further change of resistance at atmospheric pressure. After the second pressure exposure the resistance at room temperature (fluctuations through 2°) was followed at atmospheric pressure for 450 hours. The drop of resistance was at first rapid, half the total observed change occurring in the first 20 hours. Above 150 hours the rate became practically constant, with no measurable difference in the rates at 150 and 450 hours. The total drop of resistance over the 450 hours was such as to

carry the specific resistance back to a figure 8.3 per cent greater than that of the virgin material.

Less extensive observations were made on eight other compositions. These will now be described, ordered according to composition.

97.98 At per cent Bi. Observed over 2.5 hours. After exposure to 30,000 resistance at atmospheric decreased by 27.48 per cent to 0.7252 virgin. In the first hour resistance dropped slightly further to 0.7251 virgin, after which the direction of motion reversed, leaving the resistance after 2.5 hours at 0.7255 virgin. The creep was almost within the errors of observation.

89.68 At per cent Bi. Observed for 17.5 hours. Atmospheric resistance after 30,000 was 4.3 per cent below virgin. With the lapse of time resistance continued moving in the *same* direction, and at the end of 17.5 hours was 6.0 per cent below virgin. The initial rate of decrease was 39 times faster than the final rate.

79.89 At per cent Bi. Observed for 20 hours. Atmospheric resistance after 30,000 was 26.6 per cent greater than virgin; after 20 hours this had decreased to 18.6 per cent greater. The initial rate of decrease was ten to twenty times greater than the final.

63.27 At per cent Bi. Observed for 3.8 hours. The atmospheric resistance after 30,000 was 18.7 per cent greater than virgin. After 3.8 hours this had decreased to 13.2 per cent greater. The rate was approximately constant over the entire time.

19.99 per cent Bi. Observed for 8 hours. Atmospheric resistance after 30,000 was 10.0 per cent greater than virgin. After 8 hours it had dropped to 8.0 per cent greater. The initial rate was approximately twice the average over the entire time, with an intermediate episode between 2 and 3 hours when the rate decreased below average followed by a rise to above average.

10.08 per cent Bi. Observed for 8.6 hours. Atmospheric resistance after 30,000 was 3.6 per cent greater than virgin. After 8.6 hours this had dropped to 2.6 per cent greater. The rate of drop was constant after 0.7 hour; the initial rate was approximately twice the average rate.

5.07 per cent Bi. Observed over 7.67 hours. Atmospheric resistance after 30,000 was 1.15 per cent greater than virgin. After 7.67 hours this had dropped to 0.74 per cent greater. The rate of drop was approximately constant over the entire time.

2.05 *At per cent Bi*. There was no change in atmospheric resistance after 30,000 and no creep during 3.5 hours, both to one part in 13,000, the limit of sensitiveness of the readings.

There is thus a wide variation in the character of these creep phenomena, with great variations in the absolute value of velocity, with inversions in the rate of fall and even reversals in the direction of creep (in two cases). It would therefore seem probable that no one simple type of mechanism would be adequate to explain the results. In particular, the rate of nucleus formation to the stable phase is not proportional to the amount of unstable phase from which the nuclei form.

E. Electrical resistance to 100,000 kg/cm². The experimental accuracy in measuring resistances to 100,000 is of a lower order than that in measuring to 30,000, as a consequence of the necessity of transmitting pressure with a plastic rather than a true liquid. There is a further special source of error with bismuth alloys in that correction cannot be applied so as to secure agreement with previous measurements in the interval 20,000 to 30,000 because of the occurrence of bismuth transitions in this interval.

The chief interest in making the present measurements to 100,000 was to find whether there are further internal changes in addition to the formation of the compound BiSn or whether any of the high pressure bismuth transitions above 40,000 kg/cm² are accompanied in the alloys by measurable changes of resistance. It is known that the volume discontinuities of the pure bismuth transitions above 30,000 are not accompanied by measurable discontinuities of resistance.

The technique of the measurements was the same as in the former published measurements and the same apparatus was used. At first the specimens were prepared by rolling the extruded wire flat. This method of preparation produced visible imperfections and cracks and gave irregular measurements of resistance. These difficulties were avoided by squeezing the extruded wire flat between polished carboloy platens in an arbor press. The final thickness was of the order of 0.002 inch, squeezed from wire 0.020 inch in diameter.

In Figure 19 is shown the ratio of the resistance at 65,000 kg/cm² to that at 30,000, and also the ratio of resistance at 100,000 to that at 30,000. The ratios shown were given directly by the

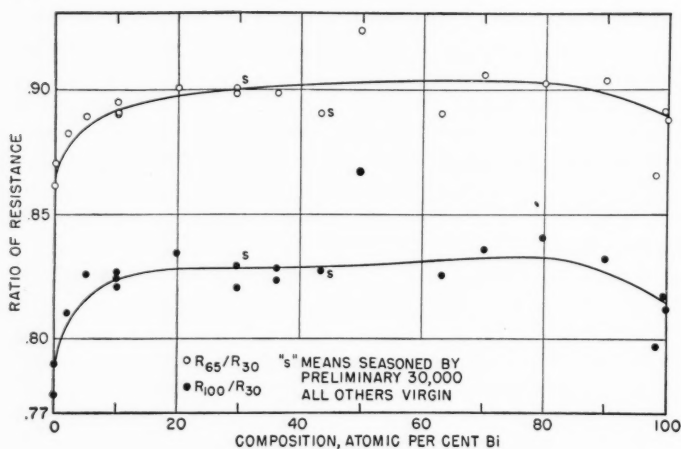


Figure 19. Summary of the resistance measurements on the bismuth-tin system to 100,000 kg/cm². The upper curve shows the ratio of resistance at 65,000 kg/cm² to the resistance at 30,000, and the lower curve the corresponding ratio for a pressure of 100,000, both as a function of composition.

readings without correction of any sort. There is considerable scatter, but no more than is characteristic of the method. In previous work four specimens of each material were measured to minimize the effect of scatter. Here, measurements were repeated only occasionally. The large number of specimens varying through a range of compositions permits an equivalent smoothing of results.

It would seem that there are no new episodes in the region above 30,000 large enough to be reflected in the behavior of resistance within the error of the method. The behavior of resistance of all compositions is normal in that it decreases with diminishing slope with increasing pressure. The arithmetical values of the pressure coefficients seem to tend to be smaller in the middle of the composition range, and the curvature of the relation between resistance and pressure greatest at the two ends of the range.

Comparison with previous results for the pure metals makes it probable that both the curves of Figure 19 are somewhat too high over their entire course.

SHEARING UNDER PRESSURE

The measurements were made with a new carboloy apparatus to be described in another place. In principle it is similar to the apparatus of steel with which extensive measurements have been made.⁶ With this new carboloy apparatus pressures of 100,000 kg/cm² are attainable as against 50,000 with the steel apparatus. In the present investigation pressure was pushed to the full 100,000 only a few times, and was usually restricted to 80,000 in the interest of longer life of the apparatus, the refiguring after use being much more exacting with carboloy than with steel.

Since the principal interest of these shearing measurements is qualitative, measurements were made on only a few compositions, namely: 100, 97.97, 79.89, 63.27, 43.4, 19.99, 10.08 At per cent Bi and 100 per cent Sn. All of the curves of shearing stress against pressure, except that for pure tin, showed a low pressure episode in the general neighborhood of 25,000 kg/cm², corresponding to the known bismuth transition here and to the irreversible formation of BiSn II near 20,000. The episode in all cases consists of a point of inflection followed by an upturn of the curve with eventual more rapid rise above 25,000 than at lower pressure. On the bismuth rich end the episode is more accentuated, consisting of a rise to a maximum, drop to a minimum, followed by accelerated rise. With diminishing bismuth content the maximum and minimum smear into each other and disappear, at the same time that the mean pressure of the episode drops approximately 5,000 kg/cm². All the curves except that of pure tin show a second episode in the general neighborhood of 65,000 kg/cm². Above this pressure shearing strength universally rises with pressure more rapidly than below. The episode is usually approached from below 65,000 by a decrease in the rate of rise and a point of inflection, although in one or two cases the preliminary decrease tends to disappear and the episode takes on more the character of a cusp. Over the middle of the composition range there is not much change in the episode, whether the composition is on the bismuth side, or whether the bismuth is entirely contained in the BiSn II phase. Bismuth is known to have a transition at 65,000; it would appear therefore that BiSn II also has a transition near the same point. The transition in pure bismuth is not accompanied by a

change in specific resistance; it would appear that the change of resistance at the BiSn transition is also small.

With regard to the absolute values of flow strength, they are small through the series, and rise from approximately equal values for pure tin and pure bismuth to a flat maximum at intermediate compositions. The value under $100,000 \text{ kg/cm}^2$ pressure is approximately $3,300 \text{ kg/cm}^2$ for the pure components, rising to $4,200$ at intermediate compositions.

X-RAY ANALYSIS

Professor Clifford Frondel of the Mineralogical Department of Harvard University most kindly undertook an X-ray examination in the effort to find the nature of the permanent change produced after exposure to high pressure, that is, to find the nature of C I. For this purpose material of 43.4 At per cent Bi — 56.6 At per cent Sn was rolled to a thickness of 0.0015 inch. One piece was exposed to $30,000 \text{ kg/cm}^2$ for approximately 15 minutes, then held at 18,500 for 20 minutes, and then pressure released to atmospheric in 5 minutes, the specimen immediately cooled to dry ice temperature and within another 5 minutes mounted in the X-ray camera where it was maintained below 0°C during the exposure of several hours. Professor Frondel describes the results as follows. The "treated" foils were those exposed to pressure as above, the "untreated" foils the controls from the same rolling.

"The treated foils appear to differ structurally from the untreated foils. I do not feel, however, that the available evidence establishes this fact conclusively. The evidence so far as it goes would be in line with a theory that the untreated foil had a disordered structure and that your treatment brought about an ordering.

"The X-ray photographs were taken in filtered copper radiation by transmission perpendicular to the surface of the foil, using the flat film method. The foils were bathed during the exposure in a stream of CO_2 from dry ice held in a funnel immediately above the sample; the sample temperature was below 0°C as shown by the development of ice at the edges of the foil (no ice was present on the area being X-rayed). Five photographs were taken: two of the untreated foils, two of the treated foils, and one of a treated foil that had been warmed almost to melting.

"The treated foils gave grainy patterns that indicated a considerable coarsening of the crystal size of the metal. The warmed foil gave a very grainy pattern, indicating a further recrystallization. The patterns of the treated and of the warmed material were identical, and they differed from that of the untreated foil in the presence of extra lines. I have not been able to determine the lattice type, symmetry or unit cell dimensions from the patterns. There were marked absorption effects on all the films."

The general conclusion would seem to be that there is not much difference between the lattices of C I and of bismuth, a conclusion in line with the volume relations. An extension of the same argument would suggest that the lattices of Bi II and C II are also similar. This means that some of the bismuth sites in the bismuth lattice can be occupied by tin without destroying the capacity of the lattice to undergo its polymorphic transitions. Under normal conditions the average atomic radius of bismuth is 9.3 per cent greater than that of tin. One would anticipate that pressure would favor the formation of a lattice of atoms of such different size.

THE BISMUTH-CADMIUM SERIES

Bismuth and cadmium are listed in works on metallurgy⁷ as being completely immiscible in all relative concentrations, so that the pressure phenomena may be expected to be especially simple. In order to check the immiscibility, an alloy was made of approximately 2 At per cent of cadmium in bismuth and the resistance measured to 30,000 kg/cm². The resistance of this alloy was not far from that of pure bismuth, and the effect of pressure on resistance not dissimilar to the effect of pressure on the resistance of pure bismuth. There was no suggestion of the anomalous behavior shown by dilute tin in bismuth. There seemed no reason therefore to question the immiscibility of the two components, and further investigation was confined to three alloys, of approximately 25, 50, and 75 At per cent. The same sort of measurements were made on these as on the bismuth-tin series, except that since no new phases were formed, many of the former phenomena did not occur, such as permanent changes after application of pressure or creep back toward virgin values.

The alloys were prepared in the same manner as before. The

same bismuth was used, and "spectroscopically pure" cadmium from the New Jersey Zinc Company.

Density. The density at room temperature, approximately 25°C, is shown in Table V and Figure 20. The variation with composition gives no suggestion of solution or compound formation, and is the sort of thing to be expected. The density at the mid point is what would be calculated assuming additive volumes.

TABLE V
DENSITY OF Bi-Cd SERIES

Composition At % Bi	Density
100.00	9.788
75.58	9.616
49.95	9.361
24.90	9.038
0.00	8.648

The density of this series has also been measured by Gabe and Evans.⁸ Their densities are consistently somewhat higher than mine; the discrepancy rises to a maximum of 0.04 on the density at the middle of the composition range.

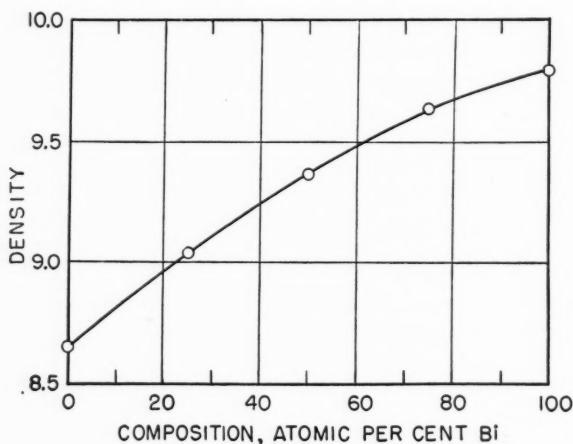


Figure 20. The density at atmospheric pressure and room temperature of the bismuth-cadmium system as a function of composition.

Compressions to 40,000 kg/cm². Measurements were made by the same method as for the Bi-Sn series. Again the alloys were sufficiently soft so that it was not necessary to use an indium sheath. Because there were no other transitions to complicate the picture it was possible to resolve the I-II and II-III transitions. In Table VI are given the relative volume compressions as a func-

TABLE VI
 $\Delta V/V_0$ TO 40,000 kg/cm² OF Bi-Cd SERIES

Pressure kg/cm ²	Composition, At %				
	100.00 Cd	75.10 Cd 24.90 Bi	50.05 Cd 49.95 Bi	24.42 Cd 75.58 Bi	100.00 Bi
5,000	0.0100	0.0124	0.0132	0.0139	0.0163
10,000	.0194	.0234	.0250	.0262	.0290
15,000	.0283	.0337	.0354	.0377	.0410
20,000	.0368	.0430	.0459	.0485	.0520
25,000	.0449	.0523	.0552	.0586	.0624
28,000		.0693	.0846	.0987	
		.0748	.0897	.1034	
		.0902	.1115	.1322	
		.0934	.1149	.1355	
30,000		.1005	.1226	.1429	.1526
35,000		.1067	.1291	.1494	.1601
40,000					.1670

tion of composition and pressure; these values are plotted in Figure 21. The data for pure cadmium were taken from previous work⁹ and run to only 25,000 kg/cm² instead of the full 40,000. At constant pressure compression varies smoothly with composition, again giving no indication of any transition or solution phenomena. This holds for the high pressure modifications as well as for the low pressure modifications. Although smooth, the compression at a fixed pressure is not a linear function of composition within limits of error. The proportional deviation from linearity tends to be greater at the lower pressures.

Electrical resistance. The same measurements were made as for the bismuth-tin series: specific resistance at atmospheric pressure, mean temperature coefficient at atmospheric pressure between room temperature and 0°C, and resistance as a function of pressure at room temperature both to 30,000 and to 100,000 kg/cm². Wires were prepared for the resistance measurements by extrusion at about 150°C to a diameter of 0.020 inch. For this the other half of the slugs that had provided the compression specimens was used.

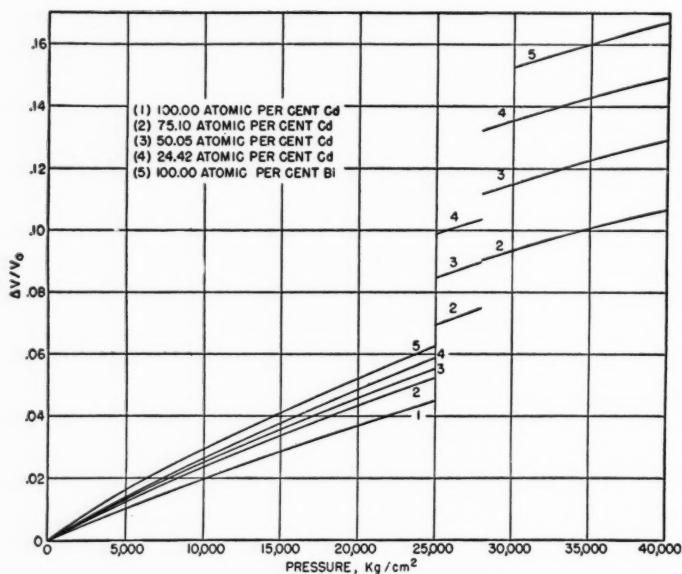


Figure 21. The volume compressions as a function of composition of the bismuth-cadmium system. Between 25,000 and 27,000 kg/cm^2 the system contains the phase Bi II, and above 27,000 the phase Bi III. The breaks in the curves correspond to the bismuth transitions.

A. *Resistance at atmospheric pressure.* The specific resistances and temperature coefficients are shown in Table VII. The specific resistance of 98 per cent bismuth is greater than the resistance of pure bismuth by a not large but nevertheless unmistakable amount, doubtless the result of lattice imperfections introduced by the cadmium impurity. Except for this, specific resistance rises smoothly from cadmium to bismuth, the rate of rise becoming rapidly greater near the bismuth end. The temperature coefficient of resistance shows no such extreme variations as in the bismuth-tin series, where there were reversals of sign, but drops at intermediate compositions below the extreme values. The drop is greatest at the bismuth end.

B. *Resistance to 30,000 kg/cm^2 .* The "specific resistances" as a function of pressure at 0° , reduced from room temperature, for

TABLE VII
RESISTANCE DATA AT ATMOSPHERIC PRESSURE FOR
Bi-Cd SERIES AT 0° C

Composition At %	Specific Resistance	Temperature Coefficient of Resistance at 0° C
100.00 Bi	$109. \times 10^{-6}$.00383
98.05	117.7	.00293
75.58	44.80	.00286
49.95	21.89	.00340
24.90	11.15	.00398
100.00 Cd	6.4	.00401

TABLE VIII
EFFECT OF PRESSURE TO 30,000 kg/cm² ON "SPECIFIC RESISTANCE"
OF Bi-Cd SERIES AT 0° C

Pressure kg/cm ²	100% Bi	98.05% Bi	"Specific Resistance" $\times 10^6$		24.90% Bi	100% Cd
			75.58% Bi	49.95% Bi		
0	109.00	117.7	44.800	21.89	11.150	6.400
5,000	119.78	130.4	44.997	21.41	10.734	6.147
10,000	131.94	144.0	45.149	20.97	10.370	5.931
15,000	145.63	160.3	45.248	20.59	10.059	5.743
20,000	160.66	175.2	45.194	20.26	9.790	5.571
25,000	178.66	192.3	44.839	19.96	9.535	5.432
	23.9 \pm	24.80	17.38	11.42	7.979	
27,000	23.7 \pm	24.54	17.07	11.34	7.813	
	98.2	63.32	28.50	15.17	8.742	
30,000		62.80	28.46	14.94	8.599	5.302

different compositions are shown in Table VIII. The "specific resistance" shown in this table is the ordinary specific resistance at atmospheric pressure multiplied at higher pressures by R_p/R_0 . That is, it is the true specific resistance uncorrected for change of dimensions under pressure. The column for pure cadmium was taken from previous measurements,¹⁰ assuming the same fractional changes at 0° as at room temperature. Again it was possible to resolve the bismuth transitions, and values are shown at 25,000 and 27,000 for the Bi II phase, and at 27,000 and 30,000 for the Bi III phase. From these figures it is possible to find the pressure coefficients of the high pressure phases, but these have relatively low accuracy because of the short pressure range and involvement with other phases. In particular, no significance should be attached to

the relative changes with composition of the pressure coefficients of the high modifications that would be calculated from the table.

The resistances of pure bismuth and the bismuth rich end of the series in the low pressure modification are not single valued in pressure, but resistance with increasing pressure on the initial application of pressure is not the same as the resistance with decreasing pressure on the final release after the transitions have occurred. The reason for this, as already indicated, is that the original orientation is not recovered after occurrence of the transitions, the low pressure form being markedly anisotropic. Since there is no definite indication of what the orientation or its change is, the best that can be done is to average resistances with increasing and decreasing pressure on the low pressure phase. There is no such uncertainty with respect to the high pressure phases, but resistances for them are single valued, except for uncertainties sometimes arising from incomplete running of a transition.

Qualitatively, the resistance of the low pressure phase behaves as would be expected. The resistance of the approximately 2 per cent Cd composition increases with pressure, and at first with increasing curvature, as does also that of pure bismuth. This curvature becomes less at higher pressures, however, and shows signs of reversing at the upper end of the pressure range. On release of pressure, resistances were a few per cent higher than on increasing pressure, with a definite tendency to drift by a small amount after every decrease of pressure. This direction of drift is downward, and is perceptible as far down as 10,000 kg/cm². It is in the opposite direction from the drift to be expected from either incomplete running of the transitions from II to I or from recovery of temperature equilibrium after the adiabatic pressure change. The only explanation which presents itself for this small drift is plastic deformations in the grains due to non-isotropic changes of dimensions after changes of pressure; there is no apparent good reason for drift down rather than drift up.

The final zero of resistance of the 75.58 per cent specimen was 6 per cent lower than that of the virgin specimen. With increasing pressure resistance was approximately constant for the first 10,000 kg/cm², followed by a decrease with increasing downward curvature. On decreasing pressure the curvature is also downward. There was a maximum resistance in the neighborhood of 20,000

followed by a decrease of approximately 2 per cent. Increasing and decreasing readings were averaged for the table.

The resistance of the 49.94 per cent specimen decreased with normal upward curvature for both increasing and decreasing pressure. The resistance with decreasing pressure was from 1.5 to 2.0 per cent lower than with increasing pressure.

The resistance of the 24.90 per cent specimen was normal in every way, the resistance dropping with upward curvature with increasing pressure and with no perceptible difference between up and down readings.

There was no evidence of a displacement of the equilibrium pressure between the high pressure modifications with changing composition. No special effort was made to establish this with maximum possible precision. This would have been increasingly difficult with increasing cadmium content because the sharpness of the transition tends to get smeared out, with progressively increasing hysteresis and widening of the pressure limits within which the transition will start with increasing and decreasing pressure. The transition from II to I with the 24.90 per cent Bi composition did not start until a pressure of about 23,000 was reached with decreasing pressure, against an equilibrium pressure of 25,000.

The ratios of the resistances when the high pressure transitions run do not vary symmetrically over the composition range. Both of these ratios of necessity drop to the limiting value unity for pure cadmium. The ratio R_I/R_{II} drops by a considerably larger factor over the composition range than does the ratio R_{II}/R_{III} , and the variation is more localized at the bismuth rich end. The former drops continuously with increasing cadmium content, whereas the latter rises to a maximum with 1.95 At per cent Cd content. The resistance of both high pressure forms is so much higher than that of pure cadmium that the net resistance of the whole system drops markedly with increasing cadmium content in the high pressure regions as well as in the region of low pressure. There was nothing here similar to the behavior of the bismuth-tin system in which one of the high pressure phases had a resistance nearly independent of composition over the entire range.

C. Resistance to 100,000 kg/cm². Measurements were made in the regular way on the three intermediate compositions. In ad-

dition, pure bismuth was specially measured again in connection with the bismuth-tin series and there are also values for both pure cadmium and pure bismuth from previously published work.¹¹ The specimens were prepared by squeezing flat between carboloy platens the extruded wire used for the resistance measurements to 30,000. The specimens showed no sign of mechanical imperfections.

Again, as in the case of the bismuth-tin series, it was not possible to correct the high pressure values so as to secure agreement with former values in the 20,000-30,000 range, but the results have to be taken at their face value.

The resistance of all specimens varied smoothly over the pressure range, with no evidence of further high pressure transitions. It would thus appear that there is no mutual solubility or compound formation in the bismuth-cadmium series, either with the usual low pressure modification of bismuth or with any of the five high pressure modifications.

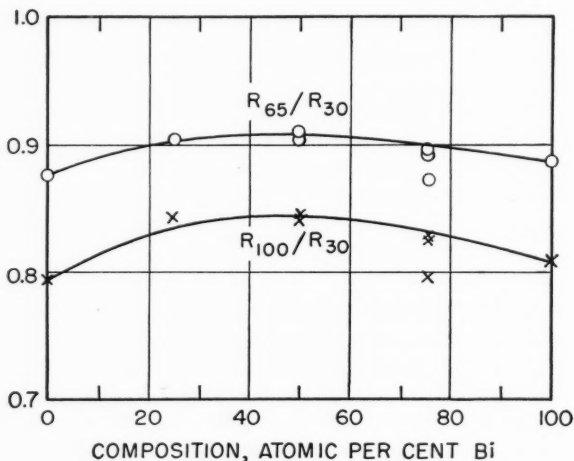


Figure 22. Summary of the resistance measurements on the bismuth-cadmium system to 100,000 kg/cm². The upper curve shows the ratio of resistance at 65,000 kg/cm² to resistance at 30,000, and the lower curve the corresponding ratio for 100,000, both as a function of composition.

The ratio of resistance at 65,000 and at 100,000 kg/cm² to the resistance at 30,000 was calculated in the same way as for the bismuth-tin series, and is shown with sufficient accuracy in Figure 22. Both ratios rise in the middle of the composition range compared with the pure components. This means a smaller absolute value for the pressure coefficient of the intermediate compositions. There is also a greater deviation from linearity in the relation between resistance and pressure in the middle of the composition range.

Shearing under pressure. Measurements were made in the regular carboly apparatus on the three intermediate compositions. The pressures were carried only to 80,000 instead of the full 100,000. All three compositions showed the expected incident accompanying the formation of the high pressure forms in the neighborhood of 25,000, diminishing in magnitude toward the cadmium end, namely diminished rate of rise of shearing strength, with point of inflection followed by more rapid rise. For the 75 and 50 At per cent bismuth compositions the rise above 25,000 continued to accelerate upwards up to the maximum pressure, but for the 25 per cent composition the curvature eventually reversed to concave downward, normal behavior for most metals. On releasing pressure on the 75 per cent specimen there was a second anomaly in the neighborhood of 45,000, presumably due to the known bismuth transition at 45,000. This is the first manifestation of this transition found in any of the measurements of this paper.

With increasing cadmium content there is at first an increase of absolute shearing strength beyond that of pure bismuth, followed by a continuous decrease. The absolute shearing strengths were, for the compositions 75, 50 and 25 At per cent Bi, 7,800, 6,600, and 4,700 kg/cm² respectively at the top pressure. These figures are materially higher than for the bismuth-tin series.

SUMMARY

The following measurements have been made on three compositions (five, counting the pure components) of the bismuth-cadmium series and approximately twenty of the bismuth-tin series: at atmospheric pressure: density, specific resistance and temperature coefficient of resistance; under pressure at room tem-

perature: volume compressions to 40,000 kg/cm², resistance to 30,000 kg/cm² under truly hydrostatic pressure and to 100,000 kg/cm² under approximately hydrostatic pressure, and occasional measurements of plastic shearing strength to 100,000 kg/cm².

The bismuth-cadmium system under normal conditions is a simple eutectic system with no appreciable solubility of either component in the other. This remains the situation under pressure, so that the properties are simple and approximately what would be expected from a mechanical mixture of the pure components. In particular the two transitions of bismuth at approximately 25,000 and 27,000 kg/cm² continue to occur independent of the presence of the other component and with no displacement of the transition pressures.

The bismuth-tin system is also under normal conditions a simple eutectic system but with mutual solubility of the two components. Under pressure, complications occur in the bismuth rich end of limited tin solubility, but no appreciable complications appear at the tin rich end, where the pressure phenomena would not suggest solubility at all. The principal complications at the bismuth rich end are connected with electrical resistance. The specific resistance increases by a factor of nearly sixfold at one per cent atomic tin. The "additive" resistance due to tin is very pressure sensitive, decreasing under pressure, whereas the resistance of pure bismuth increases. However, for very small amounts of added tin the universal rule is obeyed that the addition of a foreign component increases the pressure coefficient of resistance algebraically. The maximum pressure coefficient occurs at about one tenth atomic per cent tin. In the region of a few atomic per cent tin the total pressure effects are highly complicated, with reversals of curvature, maxima, and reversals of sign.

Beyond a few atomic per cent tin a new complication appears in the bismuth-tin system. An alloy subjected to a pressure of 25,000 kg/cm² or more experiences an irreversible change which persists on release of pressure to atmospheric with slow reversion. A study of the way in which these changes vary with composition indicates that the change consists in the formation of the compound BiSn. This compound itself has a high and a low pressure form which change into each other approximately reversibly but with some hysteresis in the range between 15,000 and 20,000 kg/cm².

The initial irreversible formation of the compound from the virgin eutectic mixture occurs only to the high pressure form and therefore only above 20,000 kg/cm². The crystal structure of the irreversibly formed product at atmospheric pressure is not known, an X-ray analysis showing only minor changes in the pattern. The volume relations are such as to indicate that in the compound the bismuth atom occupies approximately the same volume that it does in pure bismuth in that polymorphic form corresponding to the external pressure. That is, at low pressures the total volume of the system may be approximately calculated by assigning to the bismuth atom, whether in the compound or in the unaltered eutectic, the same volume that it occupies in the low pressure form of pure bismuth, and at high pressures, above 27,000 kg/cm², the total volume of the system at any composition may be approximately calculated by assigning to the bismuth atom, whether in compound or eutectic, a volume equal to the volume of the bismuth atom in pure Bi III. With regard to electrical resistance, there is a striking approximate constancy of specific resistance of the whole system, independent of composition, in the pressure range of stable existence of Bi II, this in the face of a twentyfold change in the contribution to resistance made by the Bi I-Bi II transition. The pressure of the bismuth transitions was not affected by the presence of tin. No phenomena were observed suggesting a change of solubility limits with pressure.

I am much indebted to Mr. Charles Chase for assistance in these experiments.

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